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The Third Chemical Finishing Conference

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National Cotton Council of America

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October 7-8, 1954

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National Bureau of Standards

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Foreword

The growing science of chemical finishing offers the textile industry the exciting possibility of creating new kinds of textiles in its own mills. For example, by converting the cellulose in cotton fibers, yarns, and fabrics into cellulose esters, ethers, carboxylic acids, and into nitrogen, phosphorus, titanium, and halogen derivatives, products having valuable properties for industrial, household, and apparel uses are obtained. Among these properties are enhanced resistance to mildew, heat, fire, acid, soiling, and abrasion; new dyeing characteristics; dimensional stability; crease resistance; and ability to hold a crease.

The latest developments in this active field were discussed in detail at the Chemical Finishing Conference in Washington last October. About 200 leading textile scientists, technologists, and operating executives participated. The papers on which the discussions were based ranged from reviews of compounds of potential interest, through studies of the properties of the new products, to reports on pilot-plant production of promising finishes. This conference was the third of its kind and the first for which the papers are being published by TEXTILE RESEARCH JOURNAL.

The outstanding success of the Chemical Finishing Conferences, as well as the success of the Research Clinics that have met annually in February for the past five years, is a tribute to the leadership of the National Cotton Council in initiating and sponsoring them and to the effective work of the staff of the Council, the speakers, and the session chairmen. Their contributions are appreciated by those who attended the conferences. The prompt publication of all the papers in this single issue of the JOURNAL will serve a far wider audience. It has been made possible through the cooperation of the Council, TEXTILE RESEARCH JOURNAL, and the authors.

WILLIAM D. APPEL
Chief, Textiles Section,
National Bureau of Standards

TABLE III. Properties and Quality Characteristics of Cotton*

A. Based Largely on Polymer (Cellulose) Structure

Physical Properties: tensile strength; elongation; modulus; brittleness; elasticity;† resilience;† flexibility.

Quality Characteristics: Crease resistance;† dimensional stability;† drape;† warmth;† abrasion resistance;† flex life; tear strength; permanent crispness; linting.

B. Based Largely on the Form, Dimensions, and Surface Characteristics of the Fiber

Luster;† slipperiness;† resistance to clinging;† sheerness;† wind resistance;*† resistance to soiling; resistance to transmission of gases and liquids.

C. Based Largely on Hydrophilic or Hydrophobic Characteristics‡

Water repellency;† absorbency;† quick drying;† insulating properties (electrical);† resistance to hydrolysis; dye receptivity; moisture regain; processing characteristics (static electricity).

D. Based Largely on Structure of Chemical Groups on or Attached to the Cellulose

Resistance to deterioration caused by light, oxidation, microorganisms, heat, chemicals, and irradiation; flame resistance; specific chemical reactivity; ability to copolymerize with monomers; ion-exchange properties.

* Some properties, e.g., wind resistance, crease resistance, warmth, comfort, and tear strength, are related also to fabric construction or on other factors not listed in Table III.

† Properties listed in Table II as being unusually important.

‡ Hydrophylicity and hydrophobicity, used here in the general sense, depend on several factors, including degree of crystallinity, association and swelling and the presence or absence of hydrophilic and hydrophobic groups or chemicals.

elastic properties. The numerous possibilities in this field have had inadequate effort. For example, we need better answers to the following questions: (*a*) What reagents are particularly suitable, based on their chemical properties, for the crosslinkage of cellulose? (*b*) Are short crosslinks more or less useful than long ones? (*c*) Are rigid crosslinks better than flexible ones? (*d*) What is the optimum degree of crystallinity of cellulose subjected to crosslinkage treatments? (*e*) What is the optimum degree of association?[3] (*f*) What is the effect of side groups attached to the cellulose polymer chains? (The side groups could be small ones, e.g., ethyl ether, or large ones that might be produced by graft polymerization.)

Reeves and Mazzeno [26] have rearranged certain β-glucosides to the α-form. Possibly a similar type of rearrangement with cellulose, i.e., partial or complete rearrangement of cellulose from the β-glucosidic to the α-glucosidic form, would have a beneficial effect on elastic properties, drape, resilience, etc.

Similarly, deep-seated changes in the properties of cellulose and cellulose derivatives might be effected by changing the configuration of other carbon atoms, e.g., atoms 2 and 3, in the glucose unit of cotton cellulose. One possible method for accomplishing this comprises the formation of cellulose toluenesulfonate followed by hydrolysis, ammonolysis, etc. Changes in the conformation of the glucopyranoside rings also should alter physical properties.

[3] Because of hydrogen bonding, even decrystallized cotton is highly associated.

Tear Strength and Flex Life

Theoretical considerations and limited experimental work indicate that these two properties can be improved by decrystallization, decreased association, or by a combination of the two. Either external plasticization ("softeners") or internal plasticization (side groups attached to the cellulose chain) may be used to decrease association.

Wrinkle Resistance

It is well known that chemical methods are being used commercially with some success to give cotton improved wrinkle resistance [1, 4, 23]; see also pages 20 and 24 of this issue. The method used most frequently comprises treating cotton with methylolurea, methylolmelamine, or similar chemicals followed by heat, to cause polymerization and crosslinkage. Presumably the improved elastic properties and wrinkle resistance are due to crosslinkage and increased fiber stiffness. The good effects of the treatment are accompanied by decreased tear resistance.

Drape

While fabric weight and construction and other nonchemical factors play an important role in drape, the chemical approach can be used. Decrystallization, decreased association, and a combination of these with crosslinkage also should improve drape. The attachment of unusual groups, such as the hydrophobic and oleophobic fluorocarbons, to the cellulose chains also might have a favorable effect on drape.

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[3] Because of hydrogen bonding, even decrystallized cotton is highly associated.

Tensile Strength

While nonchemical methods, e.g., mechanical processing for greater uniformity and breeding new cottons, might offer greater opportunities for increasing tensile strength than conventional chemical finishing, chemical methods, e.g., mercerization and treatment with certain amines, have already been used to effect some improvement in tensile strength.

The application of suitable plasticizers, e.g., water and certain amines, followed by stretching to effect improved orientation and increased crystallization merit additional study as a method of increasing tensile strength.

In conducting research to increase tensile strength, however, it should be remembered that for many purposes high tensile strength itself is of relatively little value unless it is accompanied by certain other properties, e.g., high flex life, suitable elastic properties, good abrasion resistance, and high tear strength.

Brittleness

Because the brittleness of cotton is attributed largely to crystallinity and extensive hydrogen bonding, it seems likely that almost any method of decreasing these will decrease brittleness. Plasticization, either internally or externally, can be expected to decrease hydrogen bonding between the cellulose chains. The common ethers and esters of cellulose are internally plasticized. Water, glycerol, etc., may be used to effect external plasticization. Thus far, satisfactory, durable external plasticizers for cotton have not been found.

Characteristics Based Largely on Fiber Form and Dimensions

It is well known that the physical shape and dimensions of the cotton fiber have an important bearing on its properties and usefulness in making yarns and fabrics. The irregularities in shape and circularity and lack of surface smoothness that characterize the cotton fiber have some advantages. For some uses, however, cotton's position could be improved by changes in surface irregularities and circularity. For example, it seems reasonable to assume that decrease in irregularity (or increased circularity and surface smoothness) would improve the following important properties: luster [9, 10], slipperiness, and resistance to soiling [7, 25].

It is known that some agents, e.g., alkali, can be used to modify some of the morphological characteristics of the cotton. These changes are frequently accompanied by improvement in luster, strength, and certain other properties. Because of the importance of fiber shape and smoothness to several key properties of cotton, research on morphological characteristics and methods to change them should be intensified. An expanded program in this field could now be undertaken under favorable circumstances because of the availability of new or improved tools, e.g., electron microscope.

Luster

Thus far, chemical methods that confer enhanced luster have been limited largely to mercerization and related treatments that leave a smoother, more lustrous surface [9, 10].

Slipperiness and Resistance to Clinging

Presumably these properties could be improved by: treatments with reagents that improve surface smoothness of cotton or protruding lint; embossing; and attachment of "lubricating" groups to the cellulose chain; fluorocarbon groups might be particularly effective.

Resistance to Soiling

It has been shown by Compton [7] and others that cotton treated with carboxymethyl cellulose and certain other polymers has improved antisoiling properties. While there is little information about other approaches to conferring antisoiling properties, it is interesting to speculate about other possibilities.

Because crevices and pits in the fiber surface facilitate some types of soiling, mercerization and similar treatments that tend to reduce surface irregularities might prove to be helpful in some instances. Increasing or decreasing the hydrophilic properties of the cotton might increase resistance to some types of soil.

Because fluorocarbons repel both polar and nonpolar materials, it seems conceivable that cellulose derivatives containing fluorocarbon groups might have unusually good antisoiling properties. The application of fluorocarbon and silicone resins to cotton also might improve the ability of cotton to resist soiling.

Characteristics Based Largely on Degree of Hydrophobicity

There is considerable information that can be used in research to increase or decrease the hydrophobic properties of cotton. Water repellency, for example, can be attained by attaching hydrophobic groups, e.g., long-chain aliphatic groups, to the cellulose chain [22, 28]. Under some conditions, a relatively low proportion of such groups can have great effect. It is reasonable to assume that the groups should be located on the surface of the fiber for maximum effectiveness. While the examples of fibrous cellulose derivatives of this general type are limited, it seems safe to conclude that this general method—attaching hydrophobic sidechains—can be used with confidence to prepare hydrophobic textile products. Even partially acetylated cotton, which has short side groups, has a moisture regain of only about 3–4% as compared with the value of 6 or 7% for cotton.

Presumably, increased hydrophobicity could be imparted to cotton also by other general methods, including crosslinkage; replacement of cellulose hydroxyl groups with hydrogen, fluorine or chlorine; the application of durable water-resistant polymers; and a combination of these methods.

Benzyl chloride and certain alkyl benzyl chlorides [17], which are inexpensive and known to react readily with cellulose, might be suitable for transforming cotton into hydrophobic textile products [31].

The application of various hydrophobic polymers to cotton, e.g., rubber, polyethylene, polyvinyl chloride, polystyrene, alkyl polyacrylates, and silicones, followed by treatments to confer insolubility and durability, would be expected to produce useful textile materials having increased resistance to water.

It should be emphasized that treatments to increase hydrophobicity probably would change other properties simultaneously. For example, long-chain alkyl groups attached to the cellulose polymer chain should—in addition to conferring hydrophobicity—decrease association between polymer chains and increase lubricity and tear strength.

For some purposes, it might be desirable to increase the hydrophylic properties. Cotton has been transformed into textile products having increased affinity for water by treatments that (*a*) swell the fiber, (*b*) lower the crystallinity, (*c*) attach a few small groups (such as methoxy) to interfere with the crystalline structure, and (*d*) attach hydrophylic groups to the cellulose chain. In some instances, the hydrophilic character has been increased—through the use of salt groups—to the point that the fibers are water soluble.

This type of transformation can be well illustrated by work at the Southern Laboratory on fibrous carboxymethyl ethers of cotton cellulose. The products (particularly the sodium salt) with a relatively low degree of substitution are more hydrophylic than cotton and have enhanced value for some applications. The sodium and similar salts of the highly substituted products are water soluble.

C. F. Goldthwait has achieved effects resembling increased hydrophylic properties—as judged by increased tendency to swell in water—by the application of the hydroxyethyl ether of cellulose. Presumably other hydrophylic polymers could be used to achieve this effect. The hydrophylic finishes might be made more durable by crosslinkage.

Electrical Characteristics

Electrical properties can be improved by increasing the hydrophobicity. For example, the insulating properties of acetylated cotton are better than those of cotton itself. The use of fluorocarbons and silicones—either by chemical attachment to cellulose chains or by application of resins—should be particularly attractive.

Quick Drying

Treatments that would increase hydrophobicity, decrease swelling, minimize surface and fiber irregularities, and/or increase crystallinity should decrease drying time. It is well known that fabric weight and construction influence drying time.

Absorbency

Absorbency can be improved by increasing the hydrophylic properties of cotton, decreasing fiber crystallinity, and having suitable yarn and yarn and fabric construction.

Miscellaneous

Decreased hydrophobicity would be expected to have the general effect of increasing chemical reactivity, affinity for many dyes, and ability to discharge static.

Characteristics Based Largely on Nature of Attached Groups

The properties involved here include resistance to deterioration caused by conditions encountered in service, e.g., those favoring changes caused by light, oxidation, hydrolysis, microbial attack, heat, chemicals, and irradiation. Resistance to these changes is particularly important for industrial applications and many clothing uses. Partial etherification and esterification have been found generally advantageous in improving the service life of cotton products where rot resistance and heat resistance are important. Treatments to enhance the hydrophobic properties of cotton should be helpful in many instances. The groups responsible for the new properties may be attached chemically to the cellulose chain or, in some instances at least, contained in materials located in or on the fibers.

Rot and Mildew Resistance

These properties have been achieved by applying certain fungicides and by converting the cotton cellulose into either ethers or esters [6, 16]. Temporary and durable effects, respectively, are produced by these two methods. For example, durable rot resistance can be attained by etherifying cotton with acrylonitrile or by esterifying with acetic anhydride. Inasmuch as many of the cellulose ethers [4] and esters thus far studied appear to have enhanced resistance to rotting, the exact nature of the groups thus introduced seems to be relatively unimportant in many instances. More important, apparently, is the act of covering or protecting the unbound cellulose hydroxyl groups in the cellulose amorphous regions and on the surface of the crystallites. It might be advantageous, however, to use etherifying and esterifying agents that will introduce fungistatic or fungicidal groups into the cellulose structure.

Cellulose treated with certain resins, e.g., methylolurea, methylolmelamine and methylolphosphonium chloride (THPC), also has some rot resistance. This effect could be due to fungicidal action of the resins, decreased swelling of the fibers, chemical combination of the resin with cellulose, or combinations of these.

Light Resistance

While there is relatively little information in this field, some speculation regarding methods for improving the light resistance of cotton seems warranted. For example, we know which wave lengths of light are most destructive and we have considerable information about the relationship between the structure of organic groups and their ability to absorb specific wave lengths [19]. By calling upon this information we should be able to protect cotton from the more damaging wave lengths through the use of sunscreening agents, i.e., the agents containing groups known to absorb the damaging wave lengths. Presumably the groups could be attached chemically to the cellulose chain or they could be made a part of a durable finish or coating.

One particular approach to improving resistance to light comprises treating cotton with appropriate derivatives of certain acids known or suspected to absorb ultraviolet light, to obtain the corresponding cellulose esters.

Goldthwait and his coworkers [20] have increased the light resistance of tobacco shade cloth by applying lead chromate, an inorganic screening agent. While certain other inorganic pigments can be used for this purpose, this general method has the general disadvantage—not always important—that the cotton is given the color of the pigment [18].

Because there are many light-screening agents and methods for applying them, reasonable optimism regarding research in the field seems justified.

Resistance to Oxidation

Resistance to oxidation is another factor in weathering. It seems safe to conclude as a working hypothesis that any modified cotton having improved resistance to the three elements of rot, light, and oxidation will also have improved resistance to weathering.

While little has been done to give cotton durable resistance to oxidation, information from other fields might prove useful in research on this subject. For example, much is known about oxidation and reduction in general and many materials are known that inhibit oxidation under some conditions. Moreover, there is much information about the relation between the structure of organic compounds and their effectiveness as antioxidants. It should be possible to attach certain antioxidants chemically to the cellulose chain or to apply antioxidants as part of a durable finish, dye or dyelike material. Guthrie has attached an antioxidant to cotton cellulose by treating cotton with 2,4-dinitrochlorobenzene followed by reduction:

[4] Some ethers, e.g., carboxymethyl, are not resistant.

$$\text{Cell—OH} + \text{ClC}_6\text{H}_3(\text{NO}_2)_2 \longrightarrow \text{Cell—OC}_6\text{H}_3(\text{NO}_2)_2 \longrightarrow \text{Cell—OC}_6\text{H}_3(\text{NH}_2)_2$$

Heat Resistance

Both the ethers and esters of cellulose have been observed to be more stable at elevated temperature than cellulose. Two products of this kind, cyanoethylated cotton and acetylated cotton, have been recommended for applications involving relatively high temperatures. Current information in this field suggests that the common ethers and esters of cellulose may generally be expected to have greater stability to heat than cellulose. Where the heat is encountered under moist and/or oxidizing conditions, it might be helpful to increase the hydrophobic characteristics and/or to attach antioxidant groups to the cellulose chain.

Research to Acquire More Scientific Information

From the foregoing, it is apparent that we need much additional information if—in research to prepare new textile materials from cotton—we wish to proceed directly to tailor-make the products having the particular properties needed for specific end uses. Several types of badly needed information are listed below. Because physical properties are so important in textile fibers and the relation between structure and physical properties of modified cellulose is so obscure, perhaps the greatest need is for more knowledge about composition and structure on one hand and physical properties of the fiber on the other.

Some of the subjects that might be investigated systematically to obtain information pertinent to cotton utilization are:

Chemical reactivity of cotton cellulose, and the relation between reactivity and other properties, e.g., maturity, thickness and variety of the fiber, and preprocessing handling and treatments.

Suitable methods for increasing the reactivity of cotton cellulose toward esterifying, etherifying, and other reagents.

Relationships, preferably quantitative, between fiber properties, i.e., physical, chemical, and textile, and the following: (*a*) Degree of substitution for important groups such as methyl, ethyl, butyl, and benzyl ethers and propionyl, butyryl, lauroyl, and stearoyl ester groups. (*b*) Distribution of the above-listed groups. (*c*) Nature and number of crosslinks. (*d*) Gross changes in polymer structure, i.e., effect of graft polymerization to attach either hydrophilic or hydrophobic polymer chains to the cellulose chain. (*e*) Changes in crystallinity and crystallite size. (*f*) Decreased association of decrystallized cotton. (*g*) Changes in configuration of the asymmetric carbons in cellulose and in conformation of the glucopyranoside group.

Development of a method of making the *n*-butyl and higher *n*-alkyl ethers of cotton cellulose.

Application of polymers and factors affecting the permanence and properties imparted by the polymer.

Relative advantages of using fiber, yarn, or fabric in applying chemical treatments.

Effects of tension applied to yarn and fabric during chemical treatment.

Information acquired in systematic investigations of the type outlined above obviously should be exceedingly useful in research aimed at transforming cotton into new and valuable textile products. After having developed new products, additional research would be needed, of course, to find efficient processing and optimum utilization methods.

Empirical Approach to New Textile Products

The empirical approach, as contemplated here, would comprise selecting reagents that are attractive—for one reason or another—using them to modify cotton, and then examining the products to ascertain their properties and probable usefulness. Reagents may be considered attractive because of their low cost, anticipated reactivity with cellulose, nontoxicity, ease of handling, etc. Because of the great importance of economics in the textile industry, it can be generalized that inexpensive reagents and low-cost textiles made from them and cotton are worthy of evaluation. Where the cost of the reagent is unusually low, e.g., ammonia at 4 cents per lb, it is ordinarily worth while to do considerable research to find suitable reaction conditions. There are many low-cost reagents that can be used to advantage in modifying cotton. For example, several reagents (e.g., acetylene, ammonia, urea, formaldehyde, methyl chloride, and ethyl chloride) cost less than about 10 cents per lb and others (e.g., acetic anhydride, allyl chloride, ethylene dichloride, chloracetic acid, ethylene oxide, propylene oxide, and phthalic anhydride) are available for less than about 20 cents per lb.

Other possibilities, too numerous to mention, are afforded by the empirical approach. For example,

many resins and high polymers [29] of diverse character—many of which can be applied in emulsion form—are now available for the treatment of cotton. It should be profitable to study some of these, particularly those that can be attached permanently to the cotton by crosslinkage, reaction with the cellulose, or by other means.

Summary

Some of the numerous opportunities for transforming cotton—through chemistry—into new textile products have been listed. Emphasis has been given to research that attempts to select reagents and techniques that should produce new textile products having certain desired properties. While this general rational approach cannot be followed successfully in all instances because of inadequate information, it can be used successfully on some occasions. Chemical companies and other organizations are conducting extensive researches on the chemical modification of cotton and other cellulosic fibers. As more and more information is made available by this research, it should become easier to select reagents and treatments that will transform cotton—at reasonable cost—into textile products having the particular properties needed for specific end uses. The achievement of this goal will, of course, greatly improve cotton's competitive position in the field of specialty fibers.

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The Improvement of Luster of Cotton

Part X: Special Swelling Treatments and Nonthermosetting Additives[1]

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Abstract

The results of swelling treatments which go beyond mercerizing at ordinary temperature indicate that there is an upper limit to the swelling of cotton, with increased luster as the objective. If this is exceeded, as it is with strong sulfuric acid or zinc chloride, and probably is with mercerization with caustic below 0°C, the luster is decreased, because the surface of the individual fiber is roughened.

Drastic shrinkage of yarn volume, combined with film formation and disappearance of fuzz, can leave the fabric very sheer and transparent, attributes often correlated with luster. Mechanical action on the plastic cellulose, or on films of cellulose or hydroxyethyl cellulose deposited from solution, can give increased luster through flattening and mechanical stabilization in the flattened form. These cellulose-affecting treatments tend to leave the fabric stiff, if they go beyond normal mercerizing.

Other additive finishes act on luster either through film formation or by stabilizing mechanical effects and controlling fabric structure. The more flexible thermoplastic resins can, with mechanical smoothing, produce an increase in the physical measurement of luster. However, this effect is less than that of mechanically smoothing the fabric without the thermoplastic resins, so the chief advantages lie in the other effects of these finishes, such as possible greater stability of the mechanical finish with the resin present.

In the higher ranges of luster, the eye can discriminate between luster arising from film formation or flattening, and the type of luster arising from yarn and fabric structure and from mercerizing.

The types of durable cotton finishes which have been examined with regard to their effects on luster in this study are: (1) Mercerizing (in the limited sense of treatment with sodium hydroxide solutions); (2) modified mercerizing, or treatments similar to mercerization aimed at increasing swelling or securing partial dissolving of the cotton fibers; (3) additive treatments depositing dissolved cellulose or cellulose derivatives on the cotton fibers; and (4) additive treatments with noncellulosic materials.

One important subgroup of noncellulosic additives, the thermosetting resins, has been considered in Part IX of this series [5].

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The thermoplastic resins which, as a general rule, are deposited on the fiber surface without either penetrating or swelling the fiber, are considered here.

Methods

The general procedure for evaluation of the effects of these treatments on luster has been to apply a process at several levels of add-on or degrees of action, with or without mechanical smoothing. The highest degree of mechanical smoothing in the present series was obtained by ironing by hand. When mechanical smoothing was to be avoided, the fabric was pressed in a flat bed press between press cloths. When fabric was treated on frames, it was given 5% stretch in each direction, whenever possible. If shrinkage from an earlier treatment prevented this stretch, the fabric was pulled as taut as possible.

The amount of material applied to the fabric is indicated as nominal add-on, calculated from solids content and wet pick-up. Actual weight changes were determined in certain cases.

The effects on luster are measured in terms of contrast ratio, which is a physical measure of the tendency to concentrate reflected light in the direction of mirror-like reflection, in comparison with the tendency to scatter light in all directions, and has been found to have a general, though not complete, correlation with luster as appreciated by observers. The methods of optical measurement have been described [6] and are shown in Figure 1. Unless otherwise noted, the warp yarns of the fabric were placed parallel to the light path, and one layer of fabric was examined, held on an open frame so that only the light reflected from the one layer was measured.

A light cotton twill fabric was used to obtain a satisfactory surface for viewing the yarns, in which warp-yarn effects would dominate, and the scattering effects due to weaving crimp and the filling yarns would be lessened. This fabric was a carded yarn, 7 oz/yd^2, 78 × 48, 2/1 twill, representative of the type of cotton fabric which is low in luster. Methods which improved the luster of this fabric can be expected to have even greater effect on fabrics designed for maximum luster.

Other properties were measured on certain materials. Stiffness is indicated by increased flexural rigidity [1] and is expressed in units of milligrams times centimeters. Air permeability is measured in cubic feet per square foot per minute, at a pressure across fabric equal to 0.5 in. water (ASTM D737–746).

Experimental Results

A. *Modified Mercerizing and Swelling Agents*

The use of swelling agents which do not add material to the fabric but only swell the fibers can be considered related to mercerization. In fact, sulfuric acid and zinc chloride were included in Mercer's patent of 1851 [13*a*]. There is a range of related treatments extending from systems which strongly swell the cellulose, softening and gelatinizing it so that the cotton hairs stick close together, through those which dissolve part of the fabric, especially the loose or exposed hairs, to those which deposit a film of dissolved cellulose. One of the applications of these processes is to produce fabrics which are clear and sheer, such as organdy or marquisette, or insect netting. This can be accomplished by rounding out the yarns, laying the fuzz, and cementing the fibers together, as well as by shrinking the yarn volume, leaving the fabric more open. These effects are accompanied by an increased stiffness in the fabric.

1. Strong Sulfuric Acid

Using the Heberlein patents [9, 10] as a guide, experiments were carried out above and below the critical concentration of sulfuric acid, alone and in combination with mercerization. Mercerization prior to acid treatment was with 23% NaOH, the optimum found for luster, but mercerizing after acid

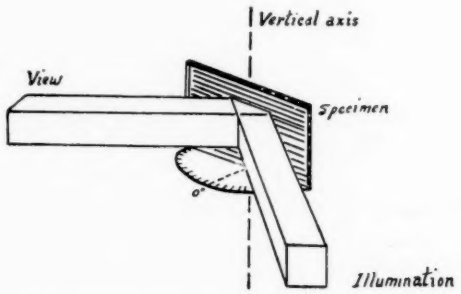

Fig. 1. Diagram indicating the beams of light. The angle of reflection, or view, and the angle of illumination are each measured between the central line of each beam and the normal (0°), which is at right angles to the general surface of the specimen. The lines drawn on the specimen can represent fibers or yarns arranged parallel to the plane of the path of the light. (*From* [6*b*].)

treatment, washing, and drying was with 32.5% caustic (38°Bé) as specified in the patents. In the treatments with acid, and the rinsing which follows (except for certain experiments with the fabric slack), the fabric was stretched on a pin frame, from which it was removed for further washing and drying. All mercerizing treatments were done with tension.

A critical point of acid concentration was near a density of 50.5°Bé, about 63% H_2SO_4. The results in Tables I and II show that in general the luster after sulfuric acid treatment was less than that after normal mercerization. Even mercerizing after the acid treatment does not raise the contrast ratio very much. Below the critical level the fabric was not stiffened to a great extent. Above the critical level, the fabric was stiffened a great deal, and in some instances the fabric became so stiff after the acid treatment that it was impossible to follow with a further mercerizing.

The general appearance of the fabric was greatly changed by the acid treatments above the critical level. During the time the cloth is wet with acid, the fibers are highly swollen, and the yarns appear jammed together. This swollen appearance continues in the wet fabric after the acid is washed out. Most of the shrinkage takes place in drying, so that, after the fabric is dried, the yarns appear separated and lean. This causes an increase of transparency and sheerness but does not give high luster. Trials with drying under tension did not increase luster, but tended to tear the fabric. The higher the acid concentration, the greater the shrinkage and the greater the increase in air permeability (Table I).

Strong sulfuric acid swells the fibers in a manner superficially similar to the swelling caused by caustic in mercerization. The swelling is also accompanied by shortening of the yarns and increased tension in fabric held at constant dimensions. However, the strong acid roughens the surfaces of the individual fibers so that shreds, which may be portions of the primary wall, hang loose from the fiber (Figure 2). These look like raised scales on hair or wool. Certain patents refer to the wool-like appearance and

TABLE I. Acid Treatment of Cotton Twill

(All treatments with tension)

Acid Conc. (°Bé)	Contrast Ratio			Flexural Rigidity			Air Permeability		
	M-A	M-A-M	A-M	M-A	M-A-M	A-M	M-A	M-A-M	A-M
52.0	1.31		1.31	+		+	564		405
51.5	1.31	1.33	1.41	+	+	396	622	452	248
51.0	1.33	1.34	1.37	+	+	471	643	499	250
50.5*	1.32	1.35	1.40	+	1410	550	616	386	241
50.0	1.37	1.37	1.40	1292	416	279	287	209	188
49.5	1.38	1.37	1.37	369	328	227	205	186	176
49.0	1.42	1.38	1.39	234	211	227	185	174	176
Merc. Control		1.43			214–339			157	
Water Control		1.30			182			78	

* = Critical level. + = Too stiff to measure (above 2000). M-A = Mercerized before acid treatment. M-A-M = Mercerized, acid treated, then mercerized. A-M = Acid treated before mercerization. Units are defined in the section on methods.

TABLE II. Acid and Mercerizing Treatments With or Without Tension

Acid Conc. (°Bé)	Condition	Contrast Ratio				Flexural Rigidity				Appearance			
		A	A-M	M-A	M-A-M	A	A-M	M-A	M-A-M	A	A-M	M-A	M-A-M
53	Tension	1.34		1.28		+		+		Mat		Mat	
53	Slack	1.26		1.27		+		+		Mat, shrunk		Mat, shrunk	
51	Tension	1.34	1.38	1.34	1.34	467	1150	993	1931	Some clearing	Clear	Clear	Clear
51	Slack	1.27	1.37	1.33	1.33	188	496	369	1355	Mat, opaque	Clear	Clear	Clear

A = Acid treatment, M = mercerized, in order shown. All mercerizations were with tension. + = Too stiff to measure (above 2000).

TABLE III. Dimensional Changes in Acid Treatment

(Mercerized control 93% warp, 105% fill)

Acid Conc. (°Bé)	Condition	A		A-M		M-A		M-A-M	
		W	F	W	F	W	F	W	F
53	Tension	93.5	92.6			95	110		
	Slack	92	88			86	99		
51	Tension	95	106	93	107	93	105	93	105
	Slack	86	102	83	104	90	104	89	104
52.0				92	103	100	99		
51.5				93	106	100	99	98	100
51.0				92	107	99	101	99	100
50.5				92	107	100	100	98	100
50.0				92	106	101	101	97	100
49.5				90	106	100	100	99	100
49.0				90	106	98	101	96	100

W = warp; F = filling; A = acid treated; M = mercerized. Dimensions after treatment as per cent of original.

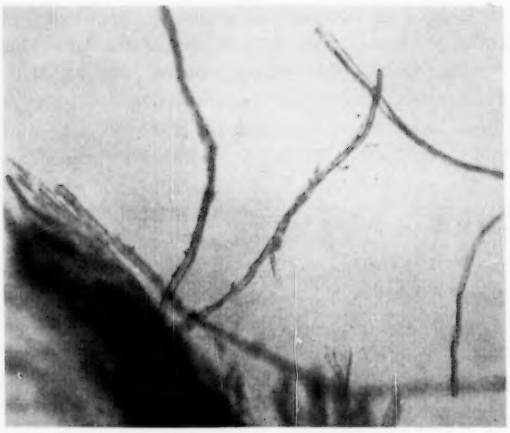

Fig. 2. Roughened surfaces of cotton fibers after treatment with sulfuric acid, 54°Bé, followed by mercerization.

handle [9], or to the whiteness of the fabric after acid treatment. This surface roughening appears to be the main basis of the mat rather than lustrous appearance of the acid-treated cotton.

One could interpret this as indicating that the swelling caused by strong sulfuric acid, perhaps combined with attack on the cellulose, goes further than that produced by caustic solutions in normal mercerizing, and ruptures the primary wall. Such rupturing has been noted by Hock [11] in examining cotton fibers swollen with cuprammonium solution. In addition to the bad effect on luster through roughening, the extreme collapse and contraction on drying is another major point of difference.

Combinations of mercerizing and acid treatment. The results of combined treatments are shown in

TABLE IV. Weight Changes in Acid Treatments

Acid Conc. (°Bé)	Treatment	Change, Dry Basis: Acid (%)	Change, Dry Basis: Merc. (%)	Moisture Regain (%)
49	A	2.23		6.24
49	AM	2.24	2.76	7.53
50.5	A	1.26		6.57
50.5	AM	1.17	1.53	7.72
51.5	A	0.85		6.82
51.5	AM	0.72	0.70	8.55
Control	Washed			5.90

A = acid treated; M = mercerized.

Tables I and II. As in other combined treatments, the greatest luster was obtained if mercerizing was the final process. However, later mercerization did not overcome the roughening.

When mercerizing or acid treatment was the first step, the fabric was stretched 5% on pin frames as usual. When one process followed the other, the fabric was stretched to an equivalent tautness, but the actual dimensions during treatment would vary with the effect of the previous treatment. Dimensions in terms of the original fabric as 100% are given in Table III for the washed fabric, pressed without tension. The greatest shrinkage observed was to 83% of original warp length, in slack treatment with 51°Bé acid. Even in treatments in which the fabric was under tension while in the acid, the warp shrank during washing and drying to 90–92% of the original length. Mercerizing before acid treatment, however, permitted the fabric to be finished at practically the original dimensions.

Weight changes in acid treatment. In view of the shrunken, almost skeletonized appearance of the

TABLE V. Luster of Commercial Fabrics, Permanent-Finish Organdy

Fabric	Thread Count W	Thread Count F	Yarn Size W	Yarn Size F	Contrast Ratio	Stiffness	Weight (oz/yd²)
A	82	67	100/1	116/1	3.62	814	1.06
B	79	67	61/1	85/1	2.50	680	1.42
C	80	70	59/1	70/1	2.30	960	1.52
D	76	69	63/1	85/1	2.35	742	1.66
E	88	80	57/1	73/1	1.78	1520	1.89

W = warp; F = filling.

TABLE VI. Effect of Zinc Chloride Treatment on Cotton Twill

Treatment	Contrast Ratio	Hand
72% $ZnCl_2$	1.21	Harsh
72% $ZnCl_2$ (mercerized)	1.14	Harsh
Control (water)	1.30	Soft
Control (mercerized)	1.43	Soft

fabric after treatment above the initial acid concentration, it is surprising that the loss in weight was so small (Table IV). The changes shown are based on the original fabric as starting material. A control, washed in the same way, lost 0.55%.

The regain column shows that the regain is increased by acid treatment, and is increased further by mercerization after acid.

Comparison with commercial fabrics. A series of organdy fabrics was purchased at retail, for comparison with the laboratory treatments. These were all rather open-texture, fine-yarn fabrics, as shown in Table V. All had a stiff hand. Under the microscope, the yarns were seen to be composed of fibers which were cemented together, like the fibers from the laboratory-treated specimens. The relatively high luster, as indicated by the contrast ratio, was attributed to the low degree of fuzz, the fineness and regularity of the yarns, and the sheerness of the fabrics. In view of the laboratory results, it was thought that this high luster came from favorable fabric structure rather than from direct effects of the acid treatment, if acid treatment had been used. Under the microscope, the individual fibers appeared cemented together in the yarns, and isolated fibers showed surface damage resembling that in Figure 2.

2. Zinc Chloride Treatments

Table VI shows the results obtained by treating cotton fabric with strong zinc chloride solutions with or without an aftertreatment in a mercerization bath.

TABLE VII. Effect of Low-Temperature Mercerization on the Contrast Ratio

Grey yarn 1.86
Water control 1.75

NaOH Conc. (%)	Temperature −10°C	0°C	+10°C	26°C
23	2.13	2.10	2.14	2.11
20	2.10	2.14	2.13	2.18
17	2.03	2.34	2.05	2.13
14	2.10	2.15	2.08	2.01
11	1.99	2.21	1.93	
8	1.94	2.00	1.83	

The results are very similar to the effects obtained by treatment with strong acids. The procedure differs from the acid treatment in that the zinc chloride solution is placed on and dried on the fabric. The final effect is created by the drying procedure as the moisture is removed from the fabric. The cotton cellulose is partially dissolved and rearranged by the treatment; but this does not result in a higher luster, rather, in a mat effect like that after strong acids. The fabric is stiffened considerably by the process. On burning, it leaves considerable ash, more than normal, mercerized, or acid-treated cotton, although the fabric had been well washed to remove salts.

Low-temperature mercerization. Low-temperature mercerization trials were carried out on yarns to allow easier manipulation in the cold, and to avoid complications of cloth structure (Table VII).

Trials were run from room temperature (26°C) down to −10°C, using natural cotton yarns which had not been bleached or kiered. The general trend was that as the temperature was lowered the concentration of caustic required to obtain similar results also decreased. However, no great advantage was obtained by the decrease in temperature. Others have concluded that the cost of refrigeration could not be met by the saving in caustic concentration [13*b*]. The highest luster was obtained with 17%

sodium hydroxide at 0°C (Table VII), and lower temperature brought a decrease in luster.

This lower luster might have been the result either of less effect or of a greater effect extending to roughening of the cell wall. The latter seems likely, since cold sodium hydroxide is known to be a solvent for cellulose [3]. Examination under the microscope shows that there is less roughening than with sulfuric acid or zinc chloride, but that there is some, and may be more, in the fibers treated at −10°C than in the fibers treated at 0°C.

3. Urea, Sodium Zincate, and Sodium Hydroxide

The combinations of the urea, zincate, and caustic have also been suggested [12] as a method of partially dissolving the fibers or of redepositing cellulose on the yarns. Trials were made of the effect of such systems on mercerized marquisette. As usual in combinations in which mercerizing is followed by other treatments, the other treatments reduced the luster. The results are shown, in terms of systematic variation of the ingredients, in Table VIII. In each trial the 6% zinc oxide gave the best results, but even after a long period of exposure the best result was slightly below the original effect obtained on mercerized cotton. These treatments may be more useful, especially for stiffening or for clearing, on cotton which has not been mercerized.

4. Cuprammonium Treatment

Since cellulose is soluble in cuprammonium hydroxide solutions, a short exposure of cotton yarns to this solution might be expected to result in swelling and possible improvement of luster. The time of action of the solvent can be controlled, the swollen or partially dissolved cellulose fixed, and the copper removed by immersing the fabric in dilute (2.5%) sulfuric acid. Examination with the microscope of yarns which had been immersed for varying periods indicated action on only the surface fibers after 30 sec. After 5 min the central fibers were still not affected, though the surface of the yarns had a coated appearance. The film was rough, and the affected fibers were roughened.

The results of trials with fabric are shown in Table IX. The luster was not improved. The stiffness had not increased greatly, but the hand was rough and harsh, indicating strong action on the superficial fibers.

TABLE VIII. Contrast Ratio of Mercerized Cotton Marquisette Treated with Urea-Zincate Solutions

Treatment	Contrast Ratio 45 sec	Contrast Ratio 18 hr
10% NaOH + 10% urea +		
2% ZnO	1.47	1.48
6% ZnO	1.53	1.47
10% ZnO	1.49	1.45
20% NaOH + 10% urea +		
2% ZnO	1.54	1.45
6% ZnO	1.50	1.49
10% ZnO	1.44	1.48
20% NaOH + 20% urea +		
2% ZnO	1.47	1.49
6% ZnO	1.54	1.57
10% ZnO	1.45	1.47
Water control	1.58	

B. *Cellulosic Additive Finishes*

Previously dissolved cellulose or hydroxyethyl cellulose can be deposited on a fabric so as to adhere to the component fibers and yarns, which are themselves swollen by the solvent. This forms a coating over the surface and with mechanical action can add a smooth sheen. The application of this type of treatment is accompanied by a stiffening of the fabric.

Cellulose in cuprammonium. In one series, cellulose pulp was dissolved in the cuprammonium. This had the same effect of decreasing luster as the plain cuprammonium solutions of Table IX, but added more stiffness, raising the flexural rigidity to 500.

Cellulose dissolved in sodium zincate. The results of procedures using "Kopan" pulp [2] are shown in Table X. The solutions were prepared according

[2] Reference to a specific product does not imply recommendation of this product over similar materials from other manufacturers.

TABLE IX. Cuprammonium Treatment of Cotton Twill

Series	Treatment time (min.)	Washings	Contrast Ratio	Flexural Rigidity
A	1	1	1.32	349
		5	1.26	245
B	1	1	1.25	243
	2	1	1.25	262
	5	1	1.24	224
Controls				
Mercerized			1.43	281
Water			1.30	182

to the manufacturer's specifications [4]. The solution with cellulose contained 7.5% sodium hydroxide and 2.25% zinc oxide when applied to the fabric. The fabric was impregnated with this cellulose solution, squeezed between rollers, stretched on a pin frame, and mercerized with 23% sodium hydroxide, to cause the cellulose to go out of solution and adhere to the fabric. This film formation was accompanied by stiffening, as well as by increased luster. The luster was increased by mechanical treatments such as hand ironing during the drying after mercerizing, or reduced by washing treatments followed by flat-bed pressing with a press cloth.

While this treatment would normally be applied to bleached fabric, a series was also carried through with premercerized fabric. In spite of the double mercerization, the luster on these preparations was not much different, so premercerization would not be recommended on either technical or economic grounds.

Hydroxyethyl cellulose. The solution for the treatment of cotton fabric was made up following the manufacturer's specifications [2] using Ceglin grade "H"[2] in 8% sodium hydroxide. This was coagulated on the fabric by a 5% sulfuric acid bath. The fabric was then thoroughly rinsed to remove excess cellulose and acid before drying. The drying procedure bonded the added cellulose ether to the cellulose of the fabric. The results obtained at various levels of add-on are shown in Table XI. The luster was increased slightly as the percent of add-on was increased, but the increase of luster was accompanied by a definite stiffening at add-ons above 2%.

Comparison with cloth which had been mercerized before treatment indicates that the gain in luster was mainly through stabilization of mechanical smoothing.

TABLE X. Contrast Ratio after Treatment with Cellulose Dissolved in Sodium Zincate

Water control 1.30 pressed, 1.44 ironed

Mercerized control 1.43 pressed, 1.52 ironed

Add-On (%)	Treatment	Contrast Ratio	Flexural Rigidity
	Bleached Cloth Series		
1	I	1.54	780
	IW	1.39	540
5	I	1.42	+
	IW	1.28	3200
	Premercerized Series		
1	I	1.48	393
	IW	1.37	389
5	I	1.44	2340
	IW	1.32	2110

I = hand ironed; W = washed after ironing, then pressed flat; + = too stiff to measure.

C. *Thermoplastic Additive Finishes*

The thermoplastic additive agents formed more or less of a film over the surface of the fibers and yarns of the fabric. At high add-ons, a coating over the whole surface would be obtained, but the present work was limited to discontinuous films. Mechanical action will produce a sheen which adds luster to the fabric. The film or spot-welding effect of these agents controlled the crimp and flatness of the yarns, and in this way will align the yarns of the fabric to give a flat surface which will increase the luster.

TABLE XI. Contrast Ratio after Treatment with Hydroxyethyl Cellulose

Water control 1.30 pressed, 1.44 ironed

Mercerized control 1.43 pressed

Add-On (%)	Treatment	Contrast Ratio	Flexural Rigidity
	Series A: Variation of Smoothing		
1.6	D	1.33	238
	T	1.31	373
	I	1.41	133
	IW	1.36	
2.6	D	1.31	+
	T	1.30	+
	I	1.50	+
	IW	1.38	
	Series B: Premercerization		
1	O	1.28	183
	M	1.40	180
3	O	1.30	2400
	M	1.44	2970
5	O	1.37	+
	M	1.46	+

D = dried on frame, almost slack; T = dried under tension on frame; I = dried nearly dry, then ironed; IW = washed after ironing, pressed with press cloth; O = ordinary; M = mercerized. All of Series *B* were pressed with a press cloth. + = too stiff to measure.

TABLE XII. Contrast Ratio and Flexural Rigidity of Cotton Twill after Thermoplastic Resin Treatment with Polyacrylic Ester (Rhoplex ER)

Treatment	Contrast Ratio			Flexural Rigidity		
Water control	1.30 pressed 1.44 ironed			182		
Mercerized control	1.43 pressed 1.52 ironed			276		
Add-On (%)	1	5	10	1	5	10
P	1.31	1.29	1.29	143	215	233
I	1.40	1.37	1.36	142	189	235
M-P	1.41	1.37	1.39	169	217	221
M-I	1.49	1.40	1.37	186	248	252

P = flat pressed; I = hand ironed; M = mercerized before treatment.

1. Acrylic Acid Esters

The acrylic ester resins formed films over the surface of the fibers which when dried and heated became permanent finishes. The films formed were described by the suppliers as very pliable and flexible. In the present tests, it was indeed found that the fabric did not become unduly stiffened or harsh. However, the luster of the fabric was increased more by mechanical action than by the actual film formation. The results of applying various levels of add-on of Rhoplex ER[2] are shown in Table XII.

Polyvinyl acetate and polyvinyl butyral resins. Tables XIII and XIV show the results of the applications of the polyvinyl resins [14, 15, 16] from emulsions, and Table XV of polyvinyl butyral from solution. These resins are thermoplastic and tend to control the fabric through a mechanical fixation of the fibers and yarns. The films did not increase the luster unless given a mechanical action to produce a smooth glossy surface which will reflect light.

The polyvinyl acetate resins have a strong stiffening effect on the fabric, while the polyvinyl butyral resin from emulsion leaves the fabric flexible. One might expect that application from solution might produce a more uniform film over the irregular fiber surface; however, the results in Table XV indicate no gain in luster over the emulsions, and much more stiffness.

Nitrile rubber latices. The nitrile elastomers [7, 8] produce a very soft, pliable film on the fabric. Hycar latex 1512[2] was used as an example. The luster was not improved by this finish. Mechanical action is again needed to produce any increase in luster, as shown in Table XVI.

TABLE XIII. Contrast Ratio of Cotton Twill after Treatment with Emulsions of Polyvinyl Acetate (KR) or Polyvinyl Butyral (BR)

Water control, P, 1.30; I, 1.44
Mercerized control, P, 1.43; I, 1.52

	KR-2*	KR-4*	BR*		BRS*	
Treatment	10%†	10%†	10%	20%†	10%	20%†
P	1.27	1.28	1.27	1.26	1.28	1.26
I	1.34	1.36	1.32	1.35	1.33	1.37
M-P	1.37	1.37	1.33	1.31	1.34	1.32
M-I	1.43	1.45	1.37	1.36	1.42	1.37

P = flat pressed; M = mercerized before treatment; I = hand ironed.

* Suppliers' designations.
† Add-on.

Ironing compared with additive finishes. The base levels of contrast ratio, for washed or water-treated controls, pressed in a flat-bed press with a press cloth, are 1.30 for bleached fabric, and 1.43 for mercerized. Ironing by hand raised the contrast ratio to 1.44 and 1.52, respectively. This indicates that the cellulose films of Table X showed more gain than simple ironing on bleached cloth, but less on mercerized. The hydroxyethyl cellulose film, at 2.6% add-on, in Table XI, also shows more gain than simple ironing, although with greatly increased stiffness.

All the types of thermoplastic resin finishes examined showed no gain in luster unless the fabric was ironed to give it a smooth mechanical finish. Such gains were smaller than the gains from ironing the untreated fabric, either plain or mercerized.

General Conclusions

The results of these various alternatives emphasize the unique nature of mercerizing, if this is defined as the process of treating with a moderate swelling agent, such as sodium hydroxide, under tension. Agents which swell more extensively, or dissolve the cellulose—even sodium hydroxide in the cold, where it has a dissolving action—act against luster by roughening the surfaces of the individual fibers. While it is conceivable that adjustment of conditions of ordinary mercerizing, and some increase of swelling, can produce improvement, there is an upper limit to the degree of swelling which is desirable for increased luster.

This does not say that the special effects of yarn compactness and stiffness are not desirable for their special purposes. The sheer transparency which arises from yarn shrinkage and clearing of fuzz has

TABLE XIV. Flexural Rigidity of Cotton Twill after Treatment with Emulsions of Polyvinyl Acetate (KR) or Polyvinyl Butyral (BR)

Water control 182
Mercerized control 276

Treatment	KR-2* 10%	KR-4* 10%	BR* 10%	BR* 20%	BRS* 10%	BRS* 20%
P	3710	2180	408	371	252	280
I	+	2510	365	340	275	278
M-P	2910	2140	310	293	211	229
M-I	+	1855	443	347	266	264

P = flat pressed; M = mercerized before treatment; I = hand ironed. + = too stiff to measure.

* Suppliers' designations.

many points of contact with luster, in the general impression of appearance of fabrics.

It is also evident that luster can be improved by film formation and by mechanical action, which flattens the fabric, reducing the crimp. The special swelling and partial solvent procedures lend themselves to producing films and stabilized mechanical changes, although usually with considerable increase in stiffness.

The approach to luster through stabilization of mechanical effects can also be secured in a limited range by use of the thermoplastic resins. However, the gains in luster are lower, for either bleached or mercerized fabric, than are obtained by similar mechanical treatments of the fabric without thermoplastic resin, so the only advantages lie in possibly greater stability of the gains obtained with the finishes present. It is probable that the thermoplastic finishes, at the levels of add-on used, are present as separate particles, so that increased scattering of light acts against the effect of smoother fabric structure.

While film formation and stabilization of structure give gains of luster in the lower range of luster, it is probable that in the higher ranges of luster more is to be gained by mercerization than by any of the additive treatments.

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TABLE XV. Effect on Cotton Twill of Polyvinyl Butyral Applied from Solution at 10% Add-On

Treatment	Contrast Ratio	Flexural Rigidity
P	1.32	2542
I	1.33	1775
M-P	1.33	1832
M-I	1.34	1325
M-control, P	1.43	281
Water control, P	1.30	182
I	1.44	

P = flat pressed; I = hand ironed; M = mercerized before treatment.

TABLE XVI. Nitrile Rubber Latex Treatment of Cotton Twill at 5% Add-On

Treatment	Contrast Ratio	Flexural Rigidity
P	1.25	176
I	1.31	201
M-P	1.31	209
M-I	1.38	224
Water control, P	1.30	182
I	1.44	
Mercerized control, P	1.43	276

P = flat pressed; M = mercerized before treatment; I = hand ironed.

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Crease-Resistant Finishes on Cotton

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AT THE first Chemical Finishing Conference of the National Cotton Council of America, the different types of chemical finishing treatments were discussed in the paper, "Review of Conventional Finishing Practices," by C. Norris Rabold; and at the second conference the mechanics of the chemical reactions of crease-resistant finishes were covered quite thoroughly by Theodore F. Cooke in his paper, "Resistance to Microbiological Degradation of Resin-Treated Cotton Fabrics." With these two papers as a background, the author thought it might be interesting to the third conference to discuss crease-resistant cottons from the standpoint of the commercial finisher and his problems.

It was only a few years ago at the close of a technical session similar to these conferences that several chemists and technical men remained for a considerable time to discuss whether there was actually any chemical reaction between materials like urea formaldehyde and melamine formaldehyde and cotton or cellulose. One group argued that there certainly was a very definite chemical reaction, while the other group insisted that the resins simply penetrated inside the fiber and then polymerized. There was considerable evidence to support the view taken by the latter group, for there appeared to be no strong chemical linkage. In cases where in processing the fabric was cured to the point where the goods were weakened or embrittled beyond commercial utility, it was only necessary to hydrolyze the resins from the fabric; the crease resistance was lost, and the original physical properties of the fabric were restored. This is probably because, with those resins, there was a much greater tendency to polymerize than to react with the cellulose molecules.

With the introduction of the modified urea formaldehyde and other chemical materials which showed a greater tendency to react with cellulose than to polymerize on continued heating, this situation changed considerably. These chemical materials gave crease resistance primarily by reacting with the cellulose. Such treating materials gave a finish which was permanent. In fact, a new era dawned in the finishing plant when this type of crease-resistant material was introduced. When finishing-plant operators found that nothing could be done to remedy the situation when they overcatalyzed or overcured a 25,000-yd lot of goods, they were filled with dismay. They protested the use of such materials even though they gave a permanent finish desirable for the ultimate consumer. They realized it was necessary to carry out their processing correctly and with precision the first time. Such a situation is comparable to that when a dyer obtains shades which he cannot strip out if he has made a bad match. However, finishers have adapted themselves to this condition, and it is now a rare occasion when a lot of crease-resistant goods is damaged in finishing.

Another factor which has been ignored in the application of crease-resistant finishes is the alkali content of the prepared goods. Practically all crease-resistant finishes used at the present time require an acid condition to catalyze them so that they react with the cotton fiber. The catalysts used for this purpose are usually of a type which are nearly neutral in the pad box. This is necessary in order to maintain stability, but these catalysts become quite acid when heated. Any alkali left in the fabric will neutralize the catalyst so that its effectiveness is lost; for example, 0.5% of an amine hydrochloride catalyst can be neutralized by 0.04% alkali as sodium hydroxide, so that, if this amount or more of caustic is left in the goods, the catalyst is entirely neutralized and, even though the standard conditions of time and temperatures for processing are followed, the reaction of the treating material with the cellulose in the fabric is not effective. This situation is quite common, because goods that are to be chemically treated are usually mercerized as a preceding step, and in very few installations is the fabric anywhere near uniform in its caustic content when coming from the mercerizers and washers. In the same manner, piece-dyed goods often come from the dyeing and washing operations with a fairly high alkalinity.

If this critical condition of alkalinity is appreciated then it is possible to sour the goods to reduce the

alkalinity or add sufficient catalyst to neutralize the alkalinity and, at the same time, leave sufficient catalyst to catalyze the chemical reaction with the cellulose. If the catalyst is fairly high in price this is an expensive method of neutralization. Regardless of the manner in which the alkalinity is handled, this is a problem which requires considerable control and checking, for there is a fundamental danger in the lack of uniformity of alkali content in the fabric to be treated. If the *p*H varies from acid to neutral to alkaline throughout a lot of goods, part of the lot is overcured, part is acceptable, and part is without fixation. Although this matter of alkalinity seems fundamental and simple it is believed probably to have caused more mystery and trouble in the application of crease-resistant finishes than any other factor.

There is another point of warning that should be mentioned. Because of the presence of phosphates or other salts, a *p*H check on fabrics to be processed is not sufficient, but a weighed amount of fabric must be titrated in water solution to determine the total alkali content as sodium hydroxide as a basis for catalyst addition.

Initially, in the production of crease-resistant cottons, there were only two commercial chemicals available for this work—urea formaldehyde and melamine formaldehyde; but as the volume of this type finish has increased during the past few years a number of additional chemical crease-resistant finishes have been produced. Just as the blending of different fibers is designed to take advantage of the desirable properties of each, so chemical treating materials can be combined to give improved properties and eliminate undesirable properties. For example, polymethylol melamine is a good crease-resistant material which has the desirable property of giving a firm but springy hand to the fabric; but, at the same time, it has a decided tendency to yellow when bleached or pressed at high temperatures. Dimethylolethylene urea likewise gives a good crease-resistant finish, but it adds practically no body to the fabric and has a tendency to hydrolyze and give unsatisfactory chlorine retention when washed at high temperatures. However, a blend of these two materials using 2¼ moles of dimethylolethylene urea with each mole of polymethylol melamine, preferably in the form of a condensation product, produces very satisfactory results on the fabric. The yellowing or browning tendency on bleaching is eliminated and the hand of the fabric is improved, and if the material treated is given a "hard cure" the chlorine retention is negligible. Finishes from this specified mole ratio will give satisfactory results, but as one departs from this definite mole ratio the favorable characteristics decrease. When we use the term "hard cure" we imply either a higher temperature, longer time of curing, or more catalyst than would be used under normal conditions.

With most treating materials the amount of chlorine retention can be greatly reduced by this hard cure, but with most treating materials the hard cure is accompanied by such a deterioration of the physical properties of the finished fabric that its use creates a hazard in commercial use.

From the standpoint of high-speed commercial production the property of migration of some materials causes considerable inconvenience. This property is probably most pronounced in the case of the melamine resins. This process is practically eliminated when the treated fabric is air dried; however, this is impracticable. It can be partially eliminated by reducing the temperatures in the tenter frames where the treated fabrics are dried. However, such a procedure may lower the speed of production from 120–150 yd/min to 50–80, which results in a great loss of production. Infrared drying is also a help in reducing migration if it is used as predrying equipment.

When we attempt to modify the cotton fiber so that it can retain all its desirable properties and at the same time acquire some of the properties of the man-made fibers, we find that one of the limiting factors is lack of thermoplasticity. The man-made fibers normally have higher crease-resistant properties; but, at the same time, because of their thermoplastic properties, they can be readily creased and pressed without interfering with the crease resistance. On the other hand, the higher the crease resistance in a cotton fabric the more difficult it is for the garment manufacturer to shape and manufacture garments. In fact, there is a very definite limit beyond which, in the present state of the art, one cannot pass without giving the garment manufacturer trouble. A crease resistance of 3.3 to 3.4 in the TBL system will give the cutter and garment manufacturer trouble. This is especially true if the fabric has a water-repellent finish in addition to crease resistance. The cutter cannot make the seams or hems lie flat. This problem will be eliminated when the Southern Regional Research or some other group finds a method for making cellulosic fibers thermoplastic.

Results of crease resistance are given in TBL

units, and this is the system Dan River Mills uses in all its laboratory work unless results in Monsanto units are demanded by a customer. Since the Monsanto testing system has been adopted almost universally, something should probably be said in defense of the use of the TBL system. All Dan River's experimental work in testing using the TBL system seems to correlate much more closely with results

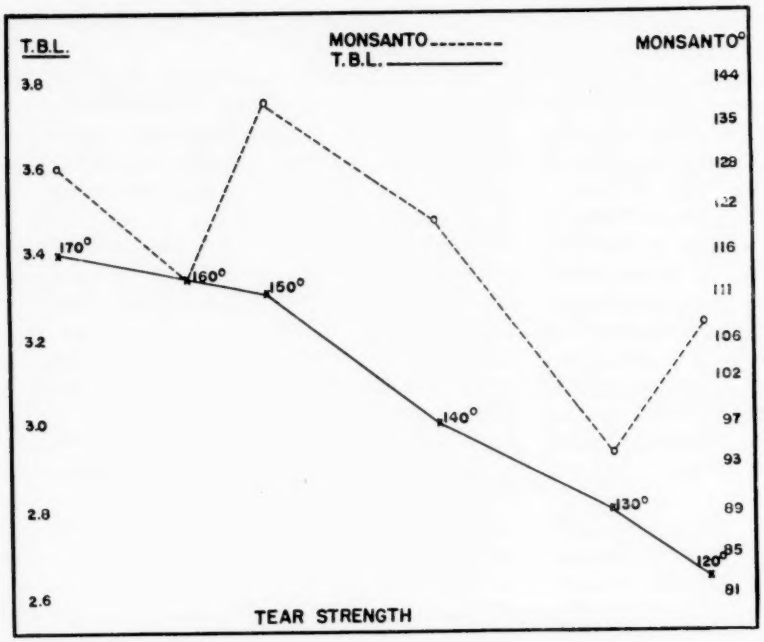

Fig. 1. TBL and Monsanto systems compared. TBL is in centimeters; Monsanto in degrees.

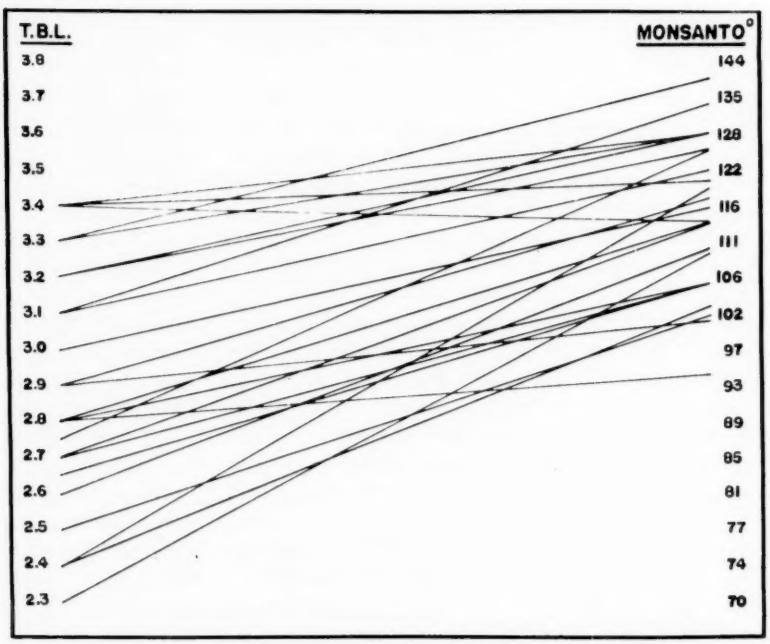

Fig. 2. One series of samples tested by two methods. TBL is in centimeters; Monsanto in degrees.

obtained on actual tests on garments. It is believed that the fact that the test strip must open up against the force of gravity comes much closer to the condition existing in a wrinkled dress than with the Monsanto system where the opening out is continually assisted by the laboratory technician. For example, with practically all the crease-resistant finishes now in use it is expected that, with higher curing temperatures, time and catalyst remaining constant, the crease resistance will improve. However, this is not confirmed by the Monsanto system of testing.

Figure 1 is typical of the values obtained when the two systems, TBL and Monsanto, are compared, on a single fabric. This is typical of hundreds of Dan River tests of this type in which time, temperature, and catalyst have been varied. On any particular series the TBL, with very few exceptions, follows consistent trends, while the Monsanto results do not follow any consistent trend. The Monsanto instrument gives a conversion table (Table I), but in Dan River experience this table gives very optimistic values when the readings are converted to the TBL system. Figure 2 shows a full series of tests which has been made on the same fabric with the same treated material where catalyst, time, and temperatures have been varied. Again, scores of comparisons of this type have been made. Note that in this large series of samples the TBL system gives a lower value than the Monsanto system, following the Monsanto conversion chart as given in Table I.

Since every chemical treating material seems to have some optimum combination of application conditions where it yields its maximum crease resistance with the least deterioration in tear strength, it has been found necessary to run a large series of experiments using different catalysts and different conditions with each treating material to find the best material and the optimum conditions of processing. Figure 3 shows the method followed in picking out the best combination for commercial processing. Since it is the spirit of this conference not to give trade names or properties, the catalysts used in this typical series of experiments have simply been numbered, and an arbitrary minimum crush-tear relationship has been set as the standard for the evaluations. Note that in this particular series of experiments

TABLE I. Monsanto Wrinkle-Recovery Tester

(Conversion Tester)

TBL (cm)	Monsanto (degrees)	TBL (cm)	Monsanto (degrees)
2.9	93	3.5	122
3.0	97	3.6	128
3.1	102	3.7	135
3.2	106	3.8	144
3.3	111	3.9	154
3.4	116	4.0	180

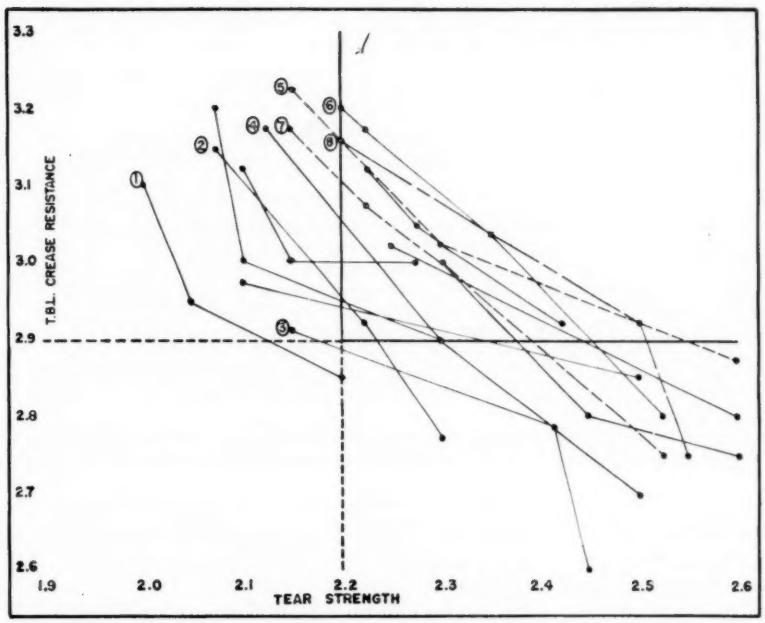

Fig. 3. Method followed in picking out the best combination for commercial processing. Dan River resin #38. Variation in catalyst and resin concentration. TBL is in centimeters; tear strength in pounds.

some catalyst-resin concentrations are entirely outside our arbitrary standard, while in other cases most of the values lie inside the desirable range. Having found the most desirable catalyst and concentration for this particular resin or chemical, a series of crease-resistant chemicals can then be compared and the best combination for the particular fabric can be selected. It is to be understood that there are other properties beside the tear strength and crease resistance which must be considered, such as migration, permanence, chlorine retention, and stabilization, before the final choice is made.

One feature might be mentioned which has added greatly to practical use of crease-resistant finishes from a commercial finisher's standpoint, and that is the stability of the present treating materials under normal storage conditions. Most of the newer materials have a shelf life of several months compared with some earlier treating materials which had to be held under cold-storage conditions; if they were left in a hot finishing plant over the week end their usability was questionable. However, the problem still remains of establishing standard conditions of procedure for all finishing equipment. The efficiency of all these treating materials is greatly affected by type of heat, direction and velocity of air currents in tenter frames and curing ovens, to the extent that only in a very general way can the times, temperatures, and other processing conditions be carried from one finishing plant to another. This situation makes the work of the technical salesman of this type treating materials very interesting and never monotonous.

Conclusion

Although there are many problems and difficulties accompanying the use of crease-resistant finishes, in the author's opinion the merits of these finishes have reached the point where the housewife will not accept fabrics without the crease-resistant finish. She appreciates the fresh appearance, the ease of laundering and pressing. The author is optimistic that the strides which have been made in chemical modification of cotton in the last few years is such that not only will cotton be able to maintain its present position, but new and desirable properties will be added through chemical means which will assist in improving its position in competition with other fibers.

Some Controversial Aspects of Crease Resistance of Cellulosic Fabrics

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Abstract

The discovery that synthetic resins could be used to improve the crease recovery of cellulosic fabrics was made on a rather empirical basis more than 25 years ago. Since that time much has been learned about synthetic resins, textile fibers, and their combination in the creaseproofing process. Yet many questions remain unanswered. This paper discusses some of the aspects of the subject that are still controversial: (*A*) Differences between cotton and rayon and the reasons therefor. Factors considered include tensile strength, tear strength, abrasion resistance, permeability of the fibers, resistance to acid hydrolysis. (*B*) A brief commentary on attempts to make cotton more like rayon. (*C*) Mechanism of crease recovery, with emphasis on the question of covalent crosslinking vs. resin formation. (*D*) Other aspects of crease resistance, emphasizing subjective characteristics such as fabric hand.

The discussion throughout is more expositional than argumentative; that is, the problems are explained, with no attempt at resolving them. A few conjectures are made where feasible.

More than a quarter century has elapsed since the discovery that cellulosic fabrics could be made more crease resistant by means of synthetic resins polymerized within the fibers [6]. This discovery—one of the most important in textile history—was of necessity made on an empirical basis, for as was pointed out by Marsh (one of the original inventors) "neither the structure of textile fibers nor of synthetic resins

was clear at the time of the crease-resisting invention" [15].

Since that time, considerable study has been made not only of textile fibers and of synthetic resins but also of their combination in the creaseproofing process. As a result, much has been learned about the nature of the changes in fabric properties brought about by the action of the various resins; and a host of papers has appeared on various phases of the subject [1, 7, 8, 10, 21, 22, 28].

Nevertheless, a number of aspects of the over-all problem have been incompletely elucidated—or are, at best, controversial. In the present discussion, we will place major emphasis on certain of the controversial aspects of crease recovery, although a number of generally accepted views will be presented to round out the picture.

By way of background, it might be well to state that creaseproofing of a cotton or rayon fabric consists, in its usual form, of impregnating the fabric with a solution of a suitable resin former or difunctional reactant, squeezing out the excess liquor, drying, and curing at an elevated temperature. The fabric should be clean and absorbent, and in the case of cotton may be premercerized. The resin may be any of a large number of monomeric reagents (generally formaldehyde derivatives) of small enough size to permit penetration into the cellulose, and capable of reacting with itself and/or with the cellulose. A suitable catalyst is added to facilitate reactivity. Afterwashing, to remove unreacted reagents, is a common practice. Aftermercerization, to improve strength properties, is less usual.

Differences between Cotton and Rayon

Both cotton and rayon are cellulosic. It is not surprising, therefore, that in general the same materials and methods which are useful in improving the crease recovery of rayon are also applicable to cotton. However, there are several differences not only in the preferred methods of handling cotton and rayon but also in the results obtained. Some of these are readily explainable on the basis of the structural differences between cotton and rayon, a few of the more apparent features of which are listed in Table I.

TABLE I. Comparison of Physical and Mechanical Properties of Rayon and Cotton Fibers

	Spun Rayon	Cotton
Staple length	At least 1.5", generally much greater	0.5–1.5" range
Cross section	Irregular but approaching circular	Resembles flattened tubes
Longitudinal appearance	Rod shape	Spirally twisted ribbon
Tensile strength	1.5–2.4 g	3–5 g
Crystallinity	30–40%	80–90%
Extensibility (orig.)	15–30%	4–6%
(resin treated)	8–12%	2–3%
Degree of polymerization	About 350	2000 or more

However, many of the observed variations in the response of cotton and rayon to resin treatment have not been completely explained on a structural basis. In the sections below, a number of differences will be pointed out, along with a few conjectures where pertinent; but without any attempt at a rigorous explanation of the phenomena.

Tensile Strength

It is well known that a cotton fabric almost invariably suffers some loss in tensile strength as a result of resin treatment, whereas rayon frequently gains in strength.

The effect will vary somewhat with type of chemical agent used. This is illustrated semiquantitatively in Figure 1, which compares the action, in altering the tensile strength of cotton and rayon fabrics, at equal solids of (*A*) a low-efficiency creaseproofing agent (one which requires a relatively high concentration to impart a given level of crease recovery), (*B*) a high-efficiency agent, and (*C*) formaldehyde. If the curves were plotted to show tensile strength as a function of crease recovery, the differences between the curves would be smaller, and curves *A* and *B* would almost coincide on cotton; nevertheless the difference between rayon and cotton would persist, as would the difference between *A* and *B* on rayon.

The loss in tensile strength is believed to be a fiber or yarn property rather than a property of the fabric. At first thought, we might regard it as primarily a

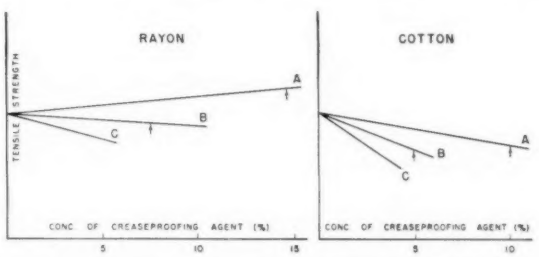


Fig. 1. General trend of tensile-strength variation as function of concentration and type of creaseproofing agent. Typical average use concentrations for types *A* and *B* are indicated by arrows.

yarn property. Thus, we might conjecture that the short staple of cotton is at least partially responsible, since the high twist necessary to form a yarn would cause severe torsional forces on the fiber when the yarn is stretched—forces which the resin-treated fiber, with its lowered elongation, would not be able to withstand. But this does not seem to be a very complete explanation, inasmuch as a spun rayon fabric of fairly short staple length and high twist will still gain strength under conditions where cotton will lose. Moreover, fabrics made of linen or ramie fibers, which are considerably longer than cotton fibers, will lose strength on resin treatment just as cotton fabrics do (see Table II).

Thus the loss is more likely a fiber property. Therefore, we might consider that the tensile loss is in some way based on the higher crystallinity of the cotton fibers. Yet Fortisan, a very crystalline rayon, shows little or no tensile loss on resin treatment. Moreover, mercerization of cotton and linen, which should lower their crystallinity, does not help to maintain tensile strength (Table II).

The true explanation is probably involved with the fine structure of rayon and cotton, in a way which is not completely clear. However, the following factors are worthy of mention:

(*a*) Cotton has so high a degree of polymerization that a single cellulose molecule can pass consecutively through several crystalline and several amorphous regions.

(*b*) Thus, when the fiber is stretched, there is little opportunity for relief of strains through slippage of the molecular chains past each other. Instead, the tension on the chains is transmitted to the numerous and relatively large crystallites, which tend to reorient in order to relieve the strain. In the view of Hermans and of Kratky [2], the amorphous regions, which comprise only a small proportion of the fiber, serve as "hinges" or "joints" around which the crystallites rotate.

(*c*) Crosslinking or resin deposition in the amorphous regions serves to immobilize the "hinges." This limits the ability of the crystallites to line up in the direction of stress, and as a result the tension is distributed over fewer molecular chains. Therefore, the resin-treated fiber ruptures at a lower stress.

(*d*) In rayon, on the other hand, the chains are much shorter, and therefore less likely to pass consecutively through several crystalline and amorphous regions.

(*e*) It is probable, too, that the transition between crystalline and amorphous areas is more gradual. Crystallites are numerous, but are not as large and well formed as in cotton, and the bulk of the fiber is in a semiordered state ranging from quite amorphous to semicrystalline.

(*f*) As a result, under tension there is a general tendency for the crystallites to rotate, but the assembly is less rigid and the forces acting on a given crystallite are less impelling than in cotton. Most important is the fact that in rayon there is greater opportunity for slippage to occur between chains, when stress cannot otherwise be relieved.

(*g*) Resin treatment of rayon, in moderation, will tend to restrict molecular reorientation, as is shown by the reduced elongation of a resin-treated fiber; but only at high concentrations, such as would saturate the extensive amorphous regions, does any appreciable strength loss occur. Moreover, in many instances there is a strength increase, probably due to a reduction in excessive interchain slippage.

(*h*) In Fortisan, which is much more crystalline than rayon, some molecular slippage is still possible due to the short chain length. This differentiates it from cotton, linen, and ramie.

TABLE II. Effect of Resin Treatment on Tensile Strength of Various Fabrics

Fiber Type	UF* Conc. (%)	Catalyst (%)	Tensile Strength (Ave. Warp+Fill) (lb) Original	Resin Treated	% Change
Rayon (spun)	10	0.5 NH_4Cl	47	51	+ 8
	15	0.5 NH_4Cl	47	55	+17
	12	0.5 Am HCl†	44	48	+ 9
	12	1 $NaHCO_3$	44	48	+ 9
	24	2 $NaHCO_3$	44	52	+18
Rayon (fil.)	12	0.5 Am HCl	177	189	+ 7
Fortisan	24	1 Am HCl	144	146	+ 1
Cotton	12	0.5 Am HCl	46	40	−13
	12	0.5 Am HCl	35	28	−20
Merc. cotton	12	0.5 Am HCl	54	43	−20
	12	0.5 Am HCl	56	41	−27
Linen	12	0.5 Am HCl	61	39	−36
Merc. linen	12	0.5 Am HCl	77	47	−39

* Urea formaldehyde. † Amine HCl.

This view is in agreement with other known facts. For example, moisture strengthens cotton by lubricating the "hinges" but weakens rayon by contributing to interchain slippage.

On the other hand it does not explain why strength loss of either cotton or rayon should occur at a lower concentration level with one resin or reactant than another. This cannot be attributed to molecular weight of the reagent except in the case of formaldehyde.

It is even more difficult to explain the relative loss in tensile strength at equal crease recovery. If we conjecture that products of type *A* (Figure 1) are primarily resin formers, and products of type *B* are primarily crosslinkers, we must conclude that resin-formers will show a marked advantage (in tensile strength at a given crease recovery) on rayon, but not on cotton.

The adverse action of formaldehyde—which excessively lowers the tensile strength not only on a solids basis but also at a given level of crease recovery—might variously be attributed to the shortness of the crosslink, or to the possibility that formaldehyde can penetrate into even the least accessible amophous areas, crosslinking and thus immobilizing them. But this is a matter for further study, especially in view of the fact that part of the loss in strength of formaldehyde treatments may be due to acid damage resulting from the low *p*H required to initiate reaction.

Tear Strength

Tear strength differs from tensile strength in that the force is so applied that the yarns are snapped one by one. This is a more complicated action than tensile testing, because it involves elongation of the fibers and yarns, as well as their strength. It has been established, for the trapezoid tear at least, that tear strength is a function of tensile strength times yarn elongation; that is, tear strength depends not only on the strength of a single yarn, but also on the number of yarns which can stretch to share the load before the first one breaks [12].

Both rayon and cotton show reduced elongation as a result of resin treatment; but because rayon gains slightly in tensile strength, whereas cotton loses, cotton might be regarded as doubly sensitive to tear loss. However, the reduction in elongation on resin treatment of both cotton and rayon is so great (50% or more) that it alone is primarily responsible for the loss in tear strength. We may therefore state, as a general rule, that both cotton and rayon fabrics suffer a sharp loss in tear strength as a result of resin treatment.

The situation is complicated by the fact that, while tear strength is affected by fiber and yarn properties, it is also influenced by fabric construction. The reason for this is that the tear strength will be increased whenever the yarns can slide closer together to reinforce each other so that more of them have to be stretched before the first one breaks.

This reinforcement hypothesis is borne out by the tendency of stiffening agents—which bond the yarns and prevent reinforcement—to reduce tear strength, while softeners or lubricants—which enhance reinforcement—tend to increase tear strength [8, 12]. The latter effect is quite evident in resin-treated rayon, the strength of which can almost invariably be restored through the use of a softener either in the resin bath or as a subsequent treatment.

With cotton, however, the benefit of a softener is widely variable; it depends, for unexplained reasons, on fabric construction (only certain selected constructions showing a marked improvement) and on the method of test (the Elmendorf tear test, for example, showing a greater effect for the softener than does the trapezoid test). Table III gives typical values for tear strength of a rayon challis and two lightweight cotton fabrics by two methods of test: the trapezoid test on Scott Inclined Plane #4, and the Elmendorf tearing test.

It will be noted that the rayon fabric shows restoration of strength on addition of softener by both tests. One cotton fabric shows a marked benefit in the Elmendorf test, while the other shows relatively little benefit by either test. Thus rayon is unlike

TABLE III. Tear Strength of Fabrics on Treatment with Resin and Softener*

	Rayon		"Unresponsive" Cotton		"Responsive" Cotton	
	Trap.	Elm.	Trap.	Elm.	Trap.	Elm.
Original tear strength	9.4	96	3.6	50	3.4	48
10% resin + 0.5% catalyst	5.4	73	1.9	34	2.4	44
10% resin, catalyst + 2% softener	8.6	105	2.0	39	2.6	60

* Trapezoid results in pounds; Elmendorf results in scale units.

cotton, and various cotton fabrics may be different from each other.

No explanation has been proposed for the distinguishing features of yarn and fabric construction which make many cotton fabrics relatively unresponsive to softener, when certain cottons and most rayons are responsive. In the "responsive" fabric above, the secret seems to be in yarn construction.

Nor has any explanation been advanced for the greater sensitivity of the Elmendorf test to the effect of softeners. This is further illustrated in Figure 2, from a published source [28]. One difference—of undetermined significance—between the methods is the speed of operation. In the trapezoid test, a load is slowly applied until the fabric tears. The tear strength thus obtained is a limiting value below which the fabric will not fail. The Elmendorf test is a ripping test. A load greater than that which the fabric can bear is suddenly applied; the tear strength thus obtained is a measure of the work done in tearing the sample.

This raises a very important question: which test is the more valuable in judging fabric strength in end use? It has been suggested, and not altogether facetiously, that the trapezoid value is useful in predicting whether the trousers of a stout gentleman will part at the seams when he slowly bends over; whereas the Elmendorf value is useful in predicting the length of the rip which would be produced if he were to snag the same trousers on a barbed-wire fence [28]. But the relative merits of the two tests in predicting the resistance to fabric failure in actual use have not been established. This is another matter which is, at best, controversial.

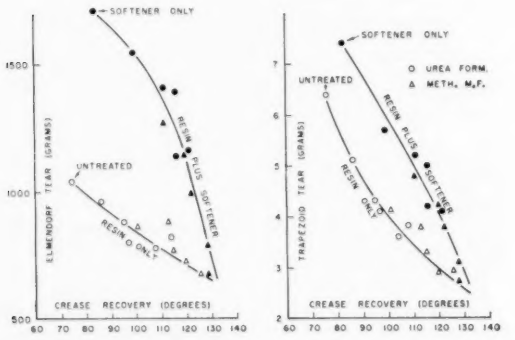


Fig. 2. Effect of softener on "responsive" cotton fabric treated with urea formaldehyde or methylated melamine formaldehyde resins.

Abrasion Resistance

On resin treatment, both rayon and cotton suffer a marked loss in abrasion resistance as measured by the usual accelerated laboratory tests [7]; and there is probably less difference in the abrasion resistance due to fiber type than there is in the different emphasis we place on this factor. That is, in rayon, where tensile and tear strength present no insurmountable difficulty, considerable attention is given to abrasion. With cotton, however, tensile and especially tear strength pose such immediate problems that there is a tendency to overlook abrasion properties.

In discussing abrasion resistance, it is difficult to be brief yet generally accurate. One reason for this is that abrasion is a single name for a variety of attritional processes. As a result, the many devices and techniques for measuring resistance to abrasion do not always correlate with each other, or with results of actual wear tests. Moreover, it has been shown [9, 24] that, on a given device, variation in the applied load may often yield widely different estimates of the abrasion resistance of a fabric. Then too, wet abrasion is quite a different property from dry abrasion [8].

In addition to the unanswered questions having to do with the relative value of the various abrasion tests, there are several other controversial aspects. Among these are:

(*a*) *The effect of surface resin.* By many methods of test—for example, those employing the TBL Ringwear, Tabor, and Schiefer devices, all of which may be considered as measuring flat abrasion—surface resins of all kinds, including both thermosetting and thermoplastic types, tend to increase abrasion resistance [25, 27, 30].

In view of the beneficial effect of surface resin on flat abrasion resistance, it might be well to consider

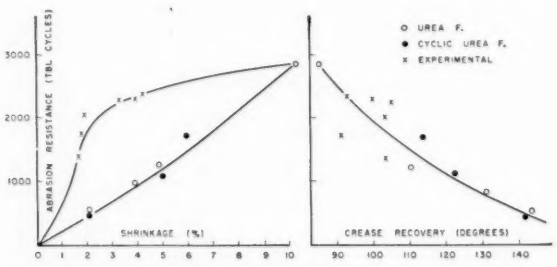


Fig. 3. Experimental resin showing superior abrasion resistance at equal stabilization but not at equal crease recovery.

certain earlier findings: Data have been published to show that certain resin formers will provide better-than-average abrasion resistance, at a given level of stabilization [8]. Unfortunately, abrasion resistance at a given level of crease recovery was not appreciably enhanced (see Figure 3). The treated fabrics were not particularly stiff, although they did have a rather full hand. It might be conjectured that part of the efficiency of the experimental resins might have been due to deposition of resin at or near the surface of the fibers, which would enhance flat abrasion resistance and impart stabilization, but fail to aid (and perhaps detract from) crease recovery. We might, in extreme instances, visualize a "case-hardened" fiber with most of the resin formation in the outer periphery.

(*b*) *The effect of long versus short crosslinks.* A similar question may be raised with regard to length of crosslink. Available evidence indicates that, at equal stabilization, long-chain crosslinkers give higher abrasion resistance and slightly poorer crease recovery than similar crosslinkers with shorter chain lengths. The observed differences may not necessarily be due to the length of crosslinks alone, but to the fact that the longer-chain molecules have not penetrated as far into the fiber. Here again, much of the crosslinking might take place in the outer periphery.

There is some question as to the effect of surface resin on flex abrasion; little published information is available. However, excessive surface resin appears to be harmful. The hypothesis has been advanced that surface resin particles act as "razor blades" which cut and damage the fiber, but experimental confirmation has not been produced.

These matters will remain highly controversial pending further study.

Permeability

Considerable work has been done on the accessibility of cotton and rayon fibers, and published data show that rayon is the more accessible of the two, not only to water (in fluid and vapor form) but also to water solutions of small molecules such as formic acid. However, in considering the permeability of cotton and rayon to larger molecules, as for example to urea formaldehyde finishing agents, such accessibility data are of little use. It is the pore size—the size of the cracks, crevices, channels, and capillaries in the fiber walls and between the amorphous areas—which limits the penetration of the larger materials, rather than the accessibility of the more nearly crystalline areas.

There is indirect evidence that, contrary to what might be supposed, the pores of cotton are larger than those of viscose rayon. Consider for example, the data of Table IV, which shows the effect on cotton and rayon fabrics of a series of resin-forming molecules of increasing molecular size. Product *A* was a typical urea formaldehyde paste of low F/U content; this was included merely to show the effect of a completely diffusible material. *B* to *F* were liquid types, similar to each other though not necessarily identical in composition; they differed primarily in the degree of condensation.

It is immediately obvious that surface effects (stiffness and poor crease recovery) are obtained sooner on rayon than on cotton as the molecular size of the resin molecule is increased.

Further evidence (see Table V) indicates that: (1) Mercerization under tension apparently lowers

TABLE IV. Effect of Increasing Particle Size on Fabric Properties

Material	Degree of Condensation	Crease Recovery (degrees)		Fabric Stiffness	
		Unmerc. Cotton	Rayon	Unmerc. Cotton	Rayon
A	Monomeric	101	113	Soft	Soft
B	Very slightly cond.	126	108	Soft	Very slightly stiff
C	Slightly cond.	127	113	Soft	Very slightly stiff
D	More cond.	124	97	Soft	Slightly stiff
E	Still more cond.	120	67	Soft	Stiff
F	Still more cond.	109	64	Soft	Stiff
Water control		61	77	Soft	Soft

TABLE V. Comparative Crease Recoveries of Various Cottons and Rayons

Fiber	Crease Recovery (degrees)	
	Untreated	Treated
Cotton	63	120, 116
Merc. cotton	53, 69, 65	111, 86
Skinless rayon	66	78, 75
Rayon	85	79, 66

Note: Each value represents a separate mercerization or resin treatment.

the effective pore size. Despite the variable test data (probably the result of uneven mercerization of small laboratory swatches), we can state that mercerized cotton is somewhat less permeable to molecules of a certain critical size than is unmercerized cotton. This may be due in part to the closing up of the lumen by mercerization. (2) The skin of normal viscose rayon fibers is not responsible for the low permeability. A "skinless" type (obtained through the courtesy of Dr. C. Schlatter and Mr. J. W. Schappel of the American Viscose Corporation) was only slightly more permeable than regular rayon.

A similar conclusion regarding the pore size of rayon and of mercerized and unmercerized cotton was reached long ago by Morton [20], who dyed various fibers from alcohol solution. Under such conditions, where the fibers could not swell, only the unmercerized cotton would pick up dye molecules above a certain size. However, all the fibers absorbed dye from water solution, indicating that the pore size was increased as the fibers swelled in water. While the size of the resin particles employed above has not been determined, they are undoubtedly larger than the dye particles employed by Morton. Thus they would not penetrate rayon even in the swollen state.

It was stated at the outset that the evidence was indirect. The conclusions have been based on the presumption that a low-molecular-weight (completely diffusible) resin former will impart crease recovery to cellulosic fabrics without stiffening them, while nondiffusible polymers will stiffen without imparting crease recovery. Staining studies—which have not been made—would be necessary to locate the resin particles in or on the fibers, and thus transfer the matter from the realm of the controversial to that of established fact.

For the present, we might consider two different concepts: The permeability of a cellulosic fiber is measured by the size of the largest particles which can penetrate into the fiber in sufficient quantity to impart a desired effect (i.e., creaseproofing, dyeing); and the accessibility of a fiber is measured by the degree to which a smaller molecule can penetrate throughout the entire fiber, including the more nearly crystalline areas. Accessibility studies with larger molecules (e.g., polyacrylic acid) might be useful in relating the two concepts.

Susceptibility to Acid Hydrolysis

Thus far, we have considered physical properties of cotton and rayon. We now turn to a chemical property—susceptibility to acid hydrolysis. However, the evidence to be presented will be that of acid damage as measured by tensile tests.

Acid damage may appear under two circumstances, (*a*) during resin treatment, and (*b*) during chlorination and ironing of the resin-treated fabric.

(*a*) *Catalysis.* It has been shown [8] that the loss in physical properties of a fabric on treatment with a thermosetting resin is due to altered stress-strain characteristics of the fibers rather than to acid hydrolysis of the cellulose. This is ordinarily the only cause of loss in the case of rayon, which rarely undergoes acid damage under normal processing conditions. But cotton is somewhat more suscepti-

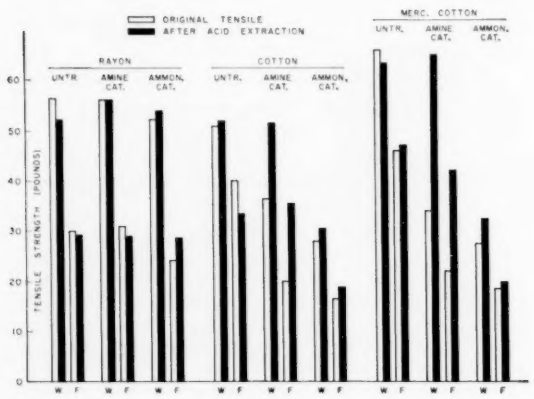


Fig. 4. Lowering of tensile strength by resin treatment, and partial or complete restoration on removal of the resin.

TABLE VI. Partial-to-Complete Recovery of Original Properties on Removal of the Crease-proofing Agent

		Ave. C. R. (degrees)		Ave. Tensile Strength (lb)	
	Catalyst	Orig.	Hyd.	Orig.	Hyd.
Rayon	*A* (Untreated)	88	80	43	41
	B Am HCl	98	81	43	42
	C NH_4Cl	119	70	38	41
Cotton	*A* (Untreated)	59	59	45	43
	B Am HCl	126	53	28	43
	C NH_4Cl	136	89	22	25
Merc. cotton	*A* (Untreated)	62	57	56	55
	B Am HCl	118	60	28	53
	C NH_4Cl	131	70	22	26

ble to acid hydrolysis, and may suffer additional loss in strength (beyond that expected from lowered elongation) under conditions which would not harm rayon.

The difference between cotton and rayon is graphically illustrated in Figure 4, which shows the lowering of warp and filling tensile strength by resin treatment, and the partial or complete restoration of original strength by careful removal of the resin. Ten per cent (solids) of a highly efficient cyclic urea formaldehyde was employed, together with either ammonium chloride or an amine hydrochloride catalyst, at a cure of 10 min at 300°F. The subsequent hydrolysis utilized 1.5% phosphoric acid and 5% urea for 20 min at 180°F, as recommended by Nickerson [21]. Table VI lists average tensile values, and also gives the corresponding crease-recovery data.

It is immediately evident that on rayon there was essentially no tensile loss, the slight loss in one case being recovered on hydrolysis of the resin. On cotton severe tensile loss occurred; where the organic amine catalyst was used, the loss was recoverable on removal of the resin, indicating no acid damage; but where ammonium chloride was used, the loss was only partially recoverable. Mercerized cotton acted similarly to unmercerized.

A few complicating factors should be mentioned. The data are atypical in that they represent a somewhat higher solids application than would normally be applied to a cotton fabric. Moreover, the crease-recovery values (Table VI) reveal that the ammonium salt-catalyzed reaction is not completely reversible on cotton, so that part of the strength loss is probably due to residual crosslinks (very likely of the methylene-bridge type, resulting from the action of free formaldehyde). Nevertheless, after due allowance for these factors, it appears evident that rayon loses little or no strength and suffers no acid damage under conditions where cotton not only loses strength but sometimes (depending on catalyst and other conditions) suffers irreversible acid damage. Moreover, mercerization does not make cotton like rayon, a factor which will be referred to later.

It should be pointed out that there are other factors, aside from the type of catalyst used, which influence the occurrence of acid damage on a given cotton or rayon fabric. The amount of catalyst is important, as are the type and amount of resin and the time and temperature of cure. The importance of catalyst concentration and curing conditions is illustrated in Table VII, which gives data on crease recovery, tensile strength, and abrasion resistance of a cotton fabric treated with 15% (solids) urea formaldehyde paste resin, plus ammonium chloride, a strong acid catalyst.

It will be observed that curing conditions are not critical at 0.1% catalyst concentration; the strength losses are quite normal. But at 0.5%, coupled with severe curing, there is an additional loss in physical properties without a compensating increase in crease recovery; this is primarily due to acid damage.

(b) Chlorination and ironing. Fabric treated with nitrogenous resins containing >NH or —NH_2 groups tend to pick up chlorine when subjected to

TABLE VII. Effect of Catalyst Concentration and Curing Conditions

Catalyst Conc. (%)	Cure		Ave. Crease Recovery (degrees)	Ave. Tensile Strength (lb)	Abrasion (TBL Cycles)
	Time (min)	Temp. (°F)			
Untreated cotton	—	—	78	38	7500
0.1	10	250	113	33	3000
0.1	10	300	113	34	3000
0.1	10	325	111	32	2900
0.5	10	250	112	33	2600
0.5	10	300	110	31	2300
0.5	10	325	112	28	1500

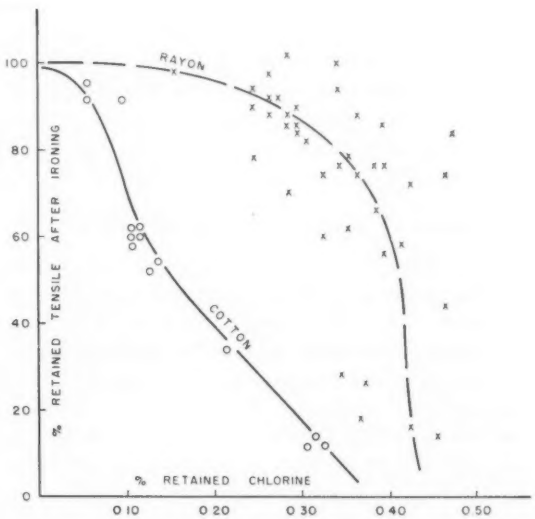


Fig. 5. Strength after chlorination and ironing of selected cotton and rayon fabrics, as a function of per cent retained chlorine.

hypochlorite bleaching baths. The chloroamine so formed (R_2NCl) is unstable to heat, and will release hydrochloric acid at high temperatures (e.g., 350° to 400°F). As a result the fabric may be weakened. It has been shown [23] that the degree of damage is a complex function of resin type, concentration, and buffering power; hypochlorite bath concentration and bath ratio; time and temperature of chlorination; and time and temperature of ironing. A complete account of the phenomenon is outside the scope of the present discussion. The important point is that, with resin type and other variables constant, cotton tends to damage at a lower level of chlorine content than does rayon. This is illustrated in Figure 5, which compares cotton and rayon fabrics treated with a cyclic urea resin, and chlorinated under increasingly severe conditions to obtain a range of chlorine pickups. On ironing at an elevated temperature (e.g., 375°F), the cotton will show severe damage at 0.10% Cl and beyond, while the rayon will withstand about three times that amount. The values are not absolute, and will vary with each particular fabric—especially in cotton—but they are typical of the marked difference between cotton and rayon in ability to withstand acid hydrolysis.

Once again, it would appear that cotton depends for its strength on the high degree of polymerization of the molecular chains. Breaking of the chains by acid hydrolysis (perhaps at very susceptible points) results in strength loss. In rayon, by contrast, the chains have already been shortened to a point where chain length is no longer a major factor; fiber strength is dependent on the orientation and intertangling of the chains during the drawing process. Thus acid hydrolysis of rayon may not only be less likely but also less harmful if it does occur.

Attempts to Make Cotton More Like Rayon

Most attempts to make cotton more amenable to creaseproofing treatments have been along one of two lines: (*a*) to decrease the degree of crystallinity by swelling treatments, such as by mercerization or by treatment with amines [31]; (*b*) to modify the cellulose structurally by reactions which will substitute bulky hydrophilic groups for some of the hydroxyls of the cellulose. Examples are carboxymethylation, hydroxyethylation, cyanoethylation, carbamylation, and phosphation. Standard resin treatments have then been made on fabrics so pretreated.

There is little doubt that a large number of investigators have taken part in such studies, even though the greatest proportion of their efforts have not been published. Conclusions to be drawn from one such unpublished study, made on cotton fabric, are as follows: (*a*) It is difficult to decrystallize cotton without allowing the fabric to shrink. Part of the strength increase—perhaps the greater part—is due to such shrinkage. (*b*) Where precautions have been taken to prevent fabric shrinkage, the fabric may still show a slight strength increase as a result of the pretreatment. (*c*) In either case, the increase in strength may be wholly or partially retained on subsequent resin treatment, or it may be completely lost; but in no case will there by any disproportionate increase in strength such as would occur if the cotton had in effect been converted into rayon.

The failure of mercerized cotton to behave like rayon has already been illustrated in Figure 4, which showed marked tensile losses on resin treatment for both mercerized and unmercerized cotton.

In another experiment, cotton fabric was impregnated for 5 min at room temperature with a 25% solution of ethylene chlorohydrin, padded, and soaked for 5 min in cold 25% sodium hydroxide solution. It was subsequently washed free of alkali, then without drying was immersed in a typical acid-catalyzed solution of urea formaldehyde paste resin, padded, dried, and cured. Dimensions were held within 6% of the original. As controls, unmercerized and mercerized cotton were also given the resin treatment. Subsequent tests (Table VIII) showed that the hydroxyethylated cotton and the mercerized cotton were both stronger than the unmercerized, but that on resin treatment, the additional strength was largely lost. Comparison of the crease recovery values likewise failed to show any advantage for the hydroxyethylated cotton.

In other instances, slight improvement in properties has resulted. But, on the basis of a number of such experiments, the controversial assertion might be ventured that such treatments do not appear to convert cotton into a new fiber having rayon-like properties, and that where advantages are obtained they are due in large measure to fabric shrinkage. Equivalent results might therefore be achieved by starting with a stronger cotton fabric in the first place.

These findings are in disagreement with published studies [3] which showed that carboxymethylated cotton fabrics will not lose strength on subsequent

resin treatment. The shrinkage of the fabric during the pretreatment was not revealed, but its probable significance is indicated by accompanying data showing that almost equivalent results could be obtained by merely premercerizing the fabric without tension.

Quite apart from the effect on tensile strength, most modified cottons lack other properties commonly associated with rayon: resistance to acid damage and to chlorine damage, and ability to increase in tear strength on treatment with softener.

It is recognized, however, that in any field so broad as that of pretreatment of cotton (in fiber, yarn, or fabric form) under a variety of conditions (time, temperature, tension) and with any of a large number of treating agents, it is too early to make general statements, and especially dogmatic ones.

Mechanism of Crease Recovery

One of the more controversial aspects of crease recovery centers around the question of crosslinking versus resin formation.

It has been well established that a creaseproofing agent penetrates into the interior of the fibers and alters the amorphous regions, but the mode of action has not been entirely clear. For several years after the invention of the TBL creaseproofing process, it was believed that a thermoset, nonyielding resin would, by its very presence, enhance recovery of the fiber. Intermolecular bonding, if considered at all, was believed to be through hydrogen bonds. Proponents of this theory made statements to the effect that there was no need to postulate the presence of covalent crosslinks [16, 33].

Cameron and Morton [1] were probably the first to point out that all effective creaseproofing agents were capable of forming covalent crosslinks, and that this was probably the mode of action. However, they stated that ". . . of a resin content of say 15%, about 1% is active in forming definite crossbonds, and the remainder is deposited interstitially in the amorphous regions of the fiber; and that the resin of both categories is effective in modifying fiber properties." They failed to state whether they believed that crease recovery was one of the properties modified by the 14% of noncrosslinking resin.

Other investigators have agreed that interchain bonding was responsible but conjectured that the bonds could be either physical or chemical in nature [8]. Still others tend to attribute the creaseproofing effect entirely to covalent crosslinks [21].

It might be stated that the question is, for the most part, academic, since it makes little practical difference how a creaseproofing agent operates. Nevertheless, an understanding of the underlying principles frequently leads to technological improvements, if not to completely new processes; and accordingly considerable study has been made of the subject.

Unfortunately, however, the problem is not simple. Consider, for example, the various reactivities of a single creaseproofing agent, such as dimethylol urea, applied to cellulose. Dimethylol urea (DMU),

$$HOCH_2NCONCH_2OH$$
$$\quad\;\;|\quad\;\;|$$
$$\quad\;\;H\quad\;\;H$$

contains two types of reactive groups, N-methylol, $>NCH_2OH$, and imido, $-\underset{\displaystyle H}{\underset{|}{N}}-$, having the following reactivities:

$$>NCH_2OH + HOCH_2N< \rightarrow >NCH_2OCH_2N< + H_2O$$

$$>NCH_2OH + HOCH_2N< \rightarrow >NCH_2N< + CH_2O + H_2O$$

$$>NCH_2OH + -NH- \rightarrow >NCH_2N< + H_2O$$

$$Cellulose-OH + HOCH_2N< \rightarrow Cellulose-O-CH_2N<$$

Based on these reactions, we may postulate at least nine modes of reaction when dimethylol urea is cured within cellulosic fibers. For convenience we will designate the dimethylol urea molecule by the symbol —M—:

TABLE VIII. Resin Treatment of Hydroxyethylated Cotton

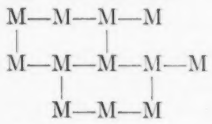
Pretreatment	Resin Treatment	Crease Recovery* (degrees)	Tensile Strength (lb)	Tear Strength† Elm.	Tear Strength† Trap.
None	None	62	35	39	2.9
	20% UF	123	28	32	1.7
Mercerized	None	65	40	46	4.3
	20% UF	112	27	35	2.3
Hydroxyethylated	None	63	40	57	4.3
	20% UF	111	28	33	2.0

* *Note:* All physical properties are average of warp and fill.
† Elmendorf results in scale units; trapezoid results in pounds.

1. Cyclic dimer $\subset \begin{matrix} M \\ M \end{matrix} \supset$

2. Linear polymer M—M—M—M—M

3. Thermoset polymer



4. Simple crosslink (see Figure 6).

5. Linear polymer, crosslinked to cellulose (Figure 6).

6. Thermoset polymer, crosslinked to cellulose (Figure 6).

7. Monomer linked to only one cellulose chain (Figure 6).

8. Linear polymer, linked to only one cellulose chain (Figure 6).

9. Thermoset polymer, linked to only one cellulose chain (Figure 6).

In the case of polymer linked to cellulose, there may be several links along the polymer chain. There is a further possibility, in any case, of obtaining a few simple methylene crosslinks from formaldehyde broken free during the cure.

Favoring the crosslinking hypothesis is the interesting fact that most creaseproofing agents can, theoretically at least, covalently crosslink cellulose [1]. This is not unusual, inasmuch as most such materials are derived from formaldehyde, the simplest creaseproofing agent, whose effect is almost certainly due to simple methylene and/or polyoxymethylene bridges [11]. And it is quite probable that when, for example, a typical urea formaldehyde monomer is applied to cellulose, some covalent crosslinking occurs; it would, in fact, be difficult to avoid. Yet resin formation must be equally likely to occur, inasmuch as most urea and melamine formaldehyde monomers will readily polymerize under less drastic conditions than those employed in curing the impregnated fabric in the typical creaseproofing process.

Another argument toward covalent crosslinking is the fact that creaseproofed fabrics are insoluble, or nearly so, in the usual cellulose solvents. The difficulty with this approach is that a series of creaseproofed fabrics, prepared with various reagents under diverse conditions of application, will show a range of solubilities (or rates of solubilities) not necessarily related to their creaseproofing efficiency. Moreover, insolubility as a measure of covalent creaseproofing would appear to be on shaky ground in view of the well-known experiment with a yarn made of polyvinyl alcohol; so long as the yarn was held under tension by a weight suspended from the lower end, it was insoluble in warm water. But when the yarn was lowered until the weight touched the bottom of the vessel, thus relaxing the tension, it dissolved. We might conclude that sufficiently strong hydrogen bonding will alter the solubility of a polymer assembly.

While it is difficult to differentiate between covalent crosslinking and hydrogen-bonded resin polymer in a creaseproofed fabric, it should be possible to adjust the conditions of treatment so that one or the other is favored. The effect on crease recovery might then give us an insight into the underlying principles. Many such experiments have been carried out, and a few of these will be described below.

One approach is based on the use of monomethylol urea (MMU) which, because it has only one reactive methylol group, presumably cannot crosslink. Therefore, if crosslinking is the sole creaseproofing mechanism, we would expect MMU to be next to worthless. In an experiment along this line, a series of urea formaldehyde monomers of varied F/U

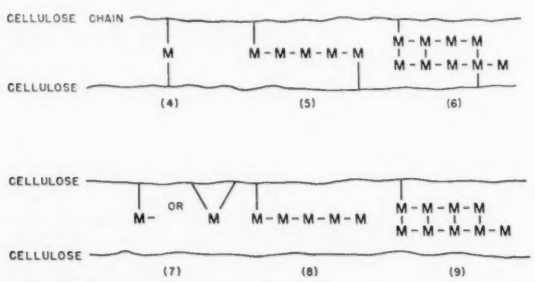


Fig. 6. Possible modes of reaction of a thermosetting resin with cellulose.

TABLE IX. Effect of Formaldehyde Ratio and Catalyst Type on Creaseproofing Efficiency

F/U Ratio	Catalyst	Crease Recovery (degrees) Rayon	Cotton
1.0	Am HCl	120	87
1.3	Am HCl	140	114
2.0	Am HCl	160	138
1.0	$NaHCO_3$	129	116
1.3	$NaHCO_3$	114	121
2.0	$NaHCO_3$	129	132
Water control		76	69

ratios were applied to cotton and rayon fabrics under acid and alkaline catalysis. The results of the study, which involved 15% solids applications plus 1% catalyst, cured 10 min at 300°, are shown in Table IX.

It is evident that the F/U ratio is of considerable importance under acid catalysis, but of relatively little importance under alkaline catalysis. At first sight, we might conjecture that, under acid catalysis, which favors the reaction of formaldehyde with cellulose, the MMU (which is monofunctional) tends to form useless dangling sidechains. Therefore, it is relatively inefficient as compared with DMU, which can readily crosslink. Under alkaline catalysis, which does not favor the reaction of formaldehyde with cellulose, MMU and DMU have nearly equal creaseproofing efficiency, presumably because they are equally capable of forming resin polymer hydrogen-bonded to the cellulose.

However, the true explanation is probably not as simple as this; no doubt a number of competing reactions occur at the same time. For example, some pyrolysis of urea can occur on alkaline cure, so that the resulting resin polymer will have a higher F/U ratio than expected. Thus MMU so applied is not necessarily monofunctional in formaldehyde. Moreover, MMU might conceivably crosslink through formation of cellulose carbamate, methylene-bridged to another cellulose molecule: Cell—O—CONH—CH_2O—Cell. Certainly no simple, unambiguous explanation of the phenomena is possible at this time.

Another approach is based on the presumption that formaldehyde will not react with cellulose at room temperature; at least, neither crease recovery nor stabilization can be obtained under any normal conditions of acid catalysis within any reasonable period of time (e.g., 10 to 20 days). Yet if a urea formaldehyde monomer is applied under such conditions, excellent results will be obtained, possibly due for the most part to polymer formation. This is illustrated in Table X, which shows the effect of a urea formaldehyde paste monomer, a cyclic urea formaldehyde monomer, and formaldehyde itself, applied to cotton fabric, air dried at room temperature, and allowed to stand for 20 days. Obviously, the fabric never dries below the conditioned moisture level, discrediting the usual belief that hot anhydrous conditions are required to effect crease recovery. Apparently all that is required is the absence of "wet" water, beyond that which serves to hydrate the cellulose.

It will be observed that the urea formaldehyde derivatives were effective in imparting crease recovery under mild acid catalysis, while formaldehyde was ineffective even though more strongly catalyzed. Poor results were obtained in the absence of catalysis and also with alkaline catalysis, although a possible incipient effect could be noted in the case of the alkaline-catalyzed UF paste. Incidentally, of the three materials, only the UF paste would be effective if cured at an elevated temperature under alkaline catalysis.

The failure to cure under alkaline catalysis at room temperature might be taken as an indication that polymer formation alone is not sufficient to provide crease recovery. However, when portions of the UF treating baths were evaporated at room temperature, the acid-catalyzed solution yielded a dry, completely insoluble resin, whereas the alkaline catalyzed solution gave a damp, semisoluble mass. This suggests therefore, that the failure of the room temperature alkaline cure to impart crease recovery is just as likely due to unsatisfactory polymer formation as it is to absence of crosslinks.

It might be argued that the inefficiency of formaldehyde at room temperature is the result of its volatility; that is, it evaporates before it can react. This is no doubt a factor; yet, even after 10 days at room temperature, sufficient formaldehyde remains in the fabric to impart dimensional stability (if not crease recovery) when the fabric is subsequently given an elevated cure. This is illustrated in Table XI, which gives data on the immediate 300° (10-min) cure, room-temperature cure, and delayed 300° cure of

TABLE X. Room-Temperature Cure of Resin-Treated Cotton

Product	Catalyst	Bath *p*H	Ave. Crease Recovery (degrees)
Water control	—	—	62
10% CH_2O (37%)	None	5.9	65
	3% Am HCl	3.5	67
	1% Na_2CO_3	10.5	68
15% MMU/DMU	None	7.4	70
	1% Am HCl	5.4	103
	1% Na_2CO_3	10.8	76
10% cyclic UF	None	7.9	62
	1% Am HCl	5.0	105
	1% Na_2CO_3	10.8	60

TABLE XI. Effect of Curing Conditions in Treating Rayon Fabrics

Treatment	Crease Recovery (degrees)					Shrinkage (%)	
	Immediate 300° Cure	Room Temperature 1 day	Room Temperature 3 days	Room Temperature 10 days	R.T. 10 Days + 300° Cure	R.T. 10 Days	R.T. 10 Days + 300° Cure
Water control	70	86	82	72	89	7.2	6.4
10% CH_2O (37%) +2% Na_2SO_4 +0.5% H_2SO_4 (to *p*H 1.3)	109	78	77	83	91	6.8	1.2
10% CH_2O (37%) +3% Am HCl	105	79	81	78	86	—	—
15% MMU/DMU +2% Am HCl	122	110	137	143	130	—	—

formaldehyde-treated fabrics. A UF paste resin treatment is included for comparison.

The failure of the residual formaldehyde to impart crease recovery can best be explained on the basis that a greater number of crosslinks are required for crease recovery than for stabilization. Yet on the basis of other evidence (Table XII), a resin former will impart recovery more quickly than stabilization.

This suggests that the loose resin polymer which is first formed will provide crease recovery, but that only when it becomes firmly set, and perhaps to some degree covalently crosslinked, will the fabric be dimensionally stable. This view is substantiated by evidence (Table XIII) that the crease recovery obtained by room-temperature curing is not quite as washfast as that resulting from an elevated cure.

In drawing conclusions based on low-temperature cure, there is one important factor which should be kept in mind: although room-temperature curing of formaldehyde does not yield crosslinks, this does not preclude the possibility of the formation of a few covalent crosslinks when a urea formaldehyde or other nitrogenous resin former is applied to cellulose under similar mild conditions. The N-methylol group (N—CH_2OH), on which the reactivity of nearly all nitrogenous resins is based, could conceivably react with cellulose under much less severe conditions than that required for the reaction of formaldehyde with cellulose. This is another of the many considerations which make difficult a clear-cut elucidation of the mechanism of crease recovery.

A third approach is based on the action of mercerizing caustic on resin-treated fabric. In one experiment, involving a fabric treated with a cyclic urea compound which has usually been regarded as reacting primarily with cellulose, it was found that mercerization without tension sharply reduced the crease recovery, but did not lower the fixed "resin" content. It is probable that the compound had polymerized somewhat, before crosslinking the cellulose (mechanism 5, Figure 6); otherwise, the long rinsing after mercerization would have washed away the detached cyclic urea fragments. The failure of the residual polymer to maintain crease recovery does not indicate that it played no part in the process, because the swelling of the cellulose by the caustic (a reagent capable of altering the crystal lattice) could conceivably disrupt hydrogen bonds between the polymer and the cellulose. In this connection, it is interesting to note that a mercerized resin-treated fabric will frequently dissolve more rapidly in a cellulose solvent than will the original untreated fabric.

Inorganic Salts

The use of borax and a few other inorganic salts to impart a temporary creaseproof effect to cellulosic

TABLE XII. Effect of Time of Cure on Crease Recovery and Dimensional Stability

Room-Temperature Cure (Days)	% Shrinkage Warp	% Shrinkage Fill	Ave. Crease Recovery (degrees)
Water control	8.3	1.9	88
1	6.9	1.3	122
5	2.2	0.6	135
10	2.1	0.6	149
20	1.9	0.0	146
Regular cure (10 min, 300°F)	1.8	0.0	130

TABLE XIII. Washfastness of Room-Temperature versus 300° Cure

Fabric	Resin (15%)	Catalyst (1%)	Room Temperature (20 days) Crease Recovery (degrees) Original	Room Temperature (20 days) Crease Recovery (degrees) Washed	Room Temperature (20 days) % Shrinkage (Warp)	300° Cure (10 min) Crease Recovery (degrees) Original	300° Cure (10 min) Crease Recovery (degrees) Washed	300° Cure (10 min) % Shrinkage (Warp)
Rayon	Water	—	85	85	9.8	76	97	8.9
	MMU/DMU	Am HCl	141	104	3.0	122	113	3.0
Cotton	Water	—	64	64	4.2	76	71	4.2
	MMU/DMU	Am HCl	108	96	1.4	118	120	0.8

fabrics is well known. It has been claimed that the effect is primarily a subjective one, showing up as a springy hand rather than as a high recovery value in the usual creasing test [17]. However, the same reference gives a table of data showing fairly good crease recovery values [18].

In a brief study of the effect of borax and other inorganic salts on a cotton sheeting and on a rayon challis, a number of earlier beliefs were confirmed and a few new facts were uncovered:

Borax is one of the few inorganic materials which improves the crease recovery of rayon fabric. The efficiency of borax is variable in magnitude, apparently depending on the exact method of application and especially on the conditions of drying [29]. This has been explained on the basis that a glassy amorphous melt must be formed within the fibers, since a crystalline deposit would be too brittle and friable to withstand repeated flexing. However, some materials which form a glassy melt (e.g., sodium silicate) are completely worthless. Among other effective materials are sodium dichromate and a few organic polyacids such as oxalic and citric acids.

As has long been recognized, glycerol improves the creaseproofing action of borax. This may be explained in two ways: (*a*) glycerol increases the acidity of boric acid, and thus facilitates the formation of a cellulose-borate compound (as proposed by Cameron and Morton [1] and others); or (*b*) glycerol increases the glassy nature of the borax film, thus insuring the presence of a springy amorphous material, rather than a fragile crystalline one, within the fibers. The effect of increasing amounts of glycerol is shown in Table XIV.

It is difficult, on the basis of these data alone, to differentiate between the theories. The optimum crease recovery of the rayon coincides with the best film properties of the creaseproofing agent, but this does not rule out the possibility that covalent crosslinking is an essential part of the process.

The most unusual effect uncovered is the failure of borax, alone or with glycerol, to creaseproof cotton. If we assume that the borax crosslinks rayon, we must conclude that it cannot crosslink cotton. On the other hand, if we assume that borax merely acts as a glassy amorphous "resin," we must conclude that, while such a polymer will be effective on rayon, some additional action (perhaps covalent crosslinking) is necessary in the case of cotton. The matter is a most controversial one at the present state of our knowledge.

Incidentally, published data [18] showing good crease recovery of cotton through such a treatment is very likely in error; the original reference [29] gives the same data under the heading of spun rayon.

Thermoplastic Polymers

From time to time investigations have been made of the possibility of improving the crease recovery of cotton and rayon through the incorporation of a rubbery polymer within the fibers. With few exceptions, the results of such studies have not been published.

Marsh [19] mentions the fact that thermoplasts are

TABLE XIV. Effect of Borax/Glycerol on Rayon and Cotton Fabrics

Treatment	Film Form	Crease Recovery (Warp) (degrees) Rayon	Crease Recovery (Warp) (degrees) Cotton
Untreated	—	91	75
8% borax	Brittle, crystalline	108	75
+2% gl.*	Brittle, glassy	113	68
+4% gl.	Hard, glassy	120	71
+6% gl.	Slightly softer, glassy	117	71
+8% gl.	Slightly tacky	114	77

* Glycerol.

inefficient in improving crease recovery. Landells and Whewell [13] have described a thorough study which showed that substantial amounts of acrylics and other resin-forming materials could be applied in monomer form and polymerized within cellulose fibers; but they do not state whether any changes in crease recovery were noted.

In an unpublished study conducted in this laboratory, acrylic monomers, as such or in solvent solution, were applied to cotton fabric, which in some cases was preswollen in water and solvent-exchanged to insure penetration of the monomer solution. Results of the study may be summarized as follows:

1. A variety of acrylic monomers may be applied to cotton fabrics and polymerized substantially within the fibers. Some surface resin is, of course, unavoidable.

2. The exact conditions of polymerization may have to be varied to suit each specific case. However, the pretreatment of the fiber with ferrous ion, as employed by Lipson and Speakman [14] on wool and by Landells and Whewell [13] on rayon, is a generally satisfactory procedure. Traces of persulfate catalyst may be added to the treating bath.

3. Neither soft, rubbery polymers (such as polyethylacrylate) nor harder polymers (such as polymethylmethacrylate) will impart crease recovery.

4. Highly polar polymers, which tend to be water soluble and which have little or no thermoplastic properties (e.g., polymethacrylamide), may impart a full, slightly springy hand effect, although much of this is likely to be due to surface resin. But crease recovery, as measured by the TBL or Monsanto test, is not appreciably improved.

5. Actual crease recovery, may, however, be obtained if the fabric containing such a polymer with reactive $—NH_2$ sidechains is given a mild formaldehyde aftertreatment. Results of one such experiment are shown in Table XV.

TABLE XV. Effect of Formaldehyde Aftertreatment on Cotton Fabrics Containing Internally Polymerized Thermoplastic

Thermoplast Present	After-treatment*	Crease Recovery (degrees)
No	No	63
No	Yes	63
Yes	No	69
Yes	Yes	119

* 5% CH_2O + 0.5% amine hydrochloride catalyst, cured 10 min at 300°F.

Again the conclusions are controversial. On the one hand, it may be conjectured that the formaldehyde converted the linear polymer to a thermoset form (i.e., crosslinked to itself), thus reducing its ability to yield or creep and improving its elastic recovery. On the other hand, the possibility cannot be ruled out that the formaldehyde crosslinked the polymer to the cellulose, even though the conditions were not sufficient to permit simple formaldehyde crosslinks.

Subjective Aspects of Crease Resistance

In nearly all discussions of creaseproofing processes and techniques, the primary emphasis is placed on delayed recovery, as measured minutes or hours or even a full day after the fabric has been sharply creased. This is no doubt as it should be, inasmuch as there is considerable evidence that a high degree of recovery by such a test usually correlates with a tendency for wrinkles to disappear when a garment is hung up overnight.

There are, however, several other criteria which must be kept in mind when formulating a crease-resisting finish. For example, it is frequently desirable that a fabric have additional body or fullness or even a little crispness. Sometimes this is intended to improve the "feel" or "handle" of the goods, while in other cases it enables the fabricated garment to better hold its shape.

Regardless of the purpose, the finish can, subjectively, be either "lively" or "dead," depending on the type of stiffening agent used, and quite aside from the actual crease recovery.

Because of the subjective nature of fabric feel and draping qualities, any discussion of the subject is on controversial ground at the outset. Nevertheless, certain factors that have been reasonably well established will be summarized below and made the basis for a few conjectures.

Resilient Stiffness

It has recently been pointed out [4, 26] that most stiffening agents can be divided into three general classes:

(*a*) *Thermoplastic.* These not only melt at high temperatures (whence their name) but also tend to creep at ordinary temperatures. The degree of stiffness imparted to the fabric will vary, depending on whether the polymer is in the glassy or rubbery state.

Glassy polymers (e.g., polyethylmethacrylate) will impart a rather stiff hand, although rarely a crisp one; but rubbery polymers (e.g., polyethylacrylate) will impart a full hand with little stiffness, because of the rapid creep of the polymer (which bonds fiber to fiber and yarn to yarn) under stress [25].

Used alone, the glassy thermoplasts sharply reduce crease recovery of cellulosic fabrics. But rubbery thermoplasts have a much smaller effect, and in fact may actually have a slight beneficial influence over the lower concentration range. Used in conjunction with standard thermosetting resin treatments, rubbery polymers will sometimes improve the crease recovery over that imparted by the thermosetting resin alone [5, 32]. The effect is most marked in a delayed recovery test, particularly as measured after 24 hr. Unfortunately, the heavy plastic hand resulting from most such treatments is frequently found to be unattractive on a subjective basis. That is, if the fabric is gently flexed (not creased) in the hands, as is customary in judging the body and stiffness of a fabric, it will be found to have a "dead" hand rather than a "lively" one. This can be explained on the basis of stress decay of the polymer bonds [4]. Theoretically it should be possible to eliminate or reduce this tendency, so that further study of such combinations of resins should not be disparaged.

(*b*) *Water-soluble polymers.* Because of the highly polar groups which confer water solubility to such a material, these polymers (in the dry state) are relatively stiff and unyielding. Accordingly they impart crispness with a fair degree of resilience, provided (1) that the humidity is not so high that the polymer is plasticized, and (2) that the fabric is not flexed to such an extent that the elastic limit of the polymer is exceeded.

Because it is impossible to avoid the second condition when the fabric is sharply creased, a high concentration of water-soluble polymer invariably reduces actual crease recovery, either instant or delayed. Therefore, such a material cannot be used alone as a crease-resistant finish.

However, it has been found that by incorporating small amounts (e.g., 1%) of a water-soluble polymer with the usual thermosetting resin or reactant, a springy stiffness is obtained without sacrifice of actual crease recovery. Moreover, the polymer is insolubilized, so that the finish has a reasonable degree of washfastness (depending to some extent on the exact constitution of the polymer).

A formulation comprising a resin, catalyst, water-soluble polymer, and a small amount of softener is commonly used in the creaseproofing of cotton fabrics.

(*c*) *Linear thermosetting polymers.* Precondensed or *B*-stage urea or melamine formaldehyde resins will impart resilient stiffening effects to cellulosic fabrics. Used in small amounts in conjunction with an internal resin or reactant they provide effects grossly comparable to those imparted by water-soluble polymers, with perhaps greater resilience, greater durability, and somewhat greater reduction in fabric strength. Here also, the exact formulation is important in determining the end result.

Wooly Hand

Another subjective factor is the full-bodied wooly hand which has long been the goal of finishers of spun rayon fabrics. It can be more nearly approached with low-efficiency urea formaldehyde resins, which are used at high concentrations (15–20% solids on weight of fabric), than with high-efficiency reactants (such as glyoxal or formaldehyde) which are employed at much lower levels—even though both types of material will impart high crease recovery values as measured by a delayed recovery test. The reason for the resilient fullness is not known; perhaps the explanation lies in the presence of bulky thermoset polymer within the fibers. Perhaps, also, the added weight exerts a subjective influence on the fabric handle. In any event, the wooliness imparted by the low-efficiency resin former cannot be equaled by the use of a high-efficiency material plus a surface resin and softener; the latter finish, while frequently satisfactory, is always thinner and less bulky.

Such a wooly feel, while required in the spun rayon field, is not yet a requirement in cotton finishing—although it is certainly a worthy goal. Unfortunately the objective is more difficult in cotton, and cannot be attained merely by selection of a certain resin former. One attempt in this direction has been through chemical modification of the cotton (phosphation, followed by mercerization) which has shown promise on a few fabric constructions. Despite the added wooliness, actual crease recovery is not significantly improved unless the fabric is subsequently resin treated.

In summary, then, we have three factors:

(*a*) Actual crease recovery, which can be obtained by bonding the cellulose molecules together within

the fiber through covalent crosslinks or, perhaps, through hydrogen bonds. It is measured by delayed recovery from an actual, sharp crease.

(*b*) Lively or resilient stiffness, which can be obtained by the use of a suitable water-soluble polymer or precondensed thermoset resin, along with the usual internal creaseproofing resin or reactant. It is measured subjectively by mildly flexing the fabric as in the usual hand evaluation. It has little in common with crease recovery, and may actually reduce it if the surface polymer is stretched to the point of cracking. Its importance lies in its beneficial effect on shape-holding properties of a garment (e.g., a blouse) as well as on customer acceptance.

(*c*) An intermediate type of resilience, which might loosely be described as a wooly fullness, whose mechanism is at present not clearly understood. It can be obtained on many spun rayon constructions through the use of a high concentration of low-efficiency resin former; but on cotton it is more difficult to attain.

Conclusion

In this lengthy discussion, we have admittedly raised many questions and answered none of them. We will, however, have fulfilled our purpose if we have done nothing more than to indicate that crease resistance is a complicated subject, and that much further study will have to be made before we can speak with assurance on some of these controversial aspects.

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Insolubility in Cuprammonium Hydroxide as a Means of Detecting Crosslinking in Chemically Modified Cotton

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Abstract

Native cellulose dissolves in cuprammonium hydroxide solution, but, when it is crosslinked, it becomes a space polymer and is insoluble in this reagent. A method of detecting alkali-stable crosslinks in cotton is presented—the sample to be tested is shaken with cuprammonium hydroxide solution for 17 hr. If it dissolves completely, cellulose chains are not crosslinked, but, if it is partially insoluble, crosslinking is indicated. Partially insoluble cellulosic material appears in the cuprammonium hydroxide as granules that are easily detected visually.

Cellulose was reacted with compounds which contained one or more groups that are reactive toward cellulose. In all cases the cellulosic derivatives made from cellulose and compounds that could crosslink it were partially insoluble in cuprammonium hydroxide. The compounds that were not capable of crosslinking cellulose produced derivatives soluble in cuprammonium hydroxide.

Cotton was made insoluble in cuprammonium hydroxide by reacting it with formaldehyde, glyoxal, chloroethylsulfuric acid, α,γ-glycerol dichlorohydrin, a mixture of α,β- and α,γ-glycerol dichlorohydrin, tetrakis(hydroxymethyl)phosphonium chloride, compounds containing two or more N-methylol groups, 1,4-disulfato-2-butyne, and potassium (disulfatoethyl) amine. Aminized cotton, which is soluble in cuprammonium hydroxide, was made insoluble by crosslinking it with either formaldehyde or tetrakis(hydroxymethyl)phosphonium chloride.

Cotton cellulose can be dispersed or dissolved in a number of electrolytic reagents. Quaternary ammonium bases such as dimethyldibenzylammonium hydroxide and trimethylbenzylammonium hydroxide dissolve cellulose. Other solvents for cellulose include phosphoric acid, sulfuric acid, copper ethylenediamine, and cuprammonium hydroxide. The last reagent is a well-known solvent for cellulose. Cellulose can be dissolved in it and then precipitated essentially without changing the cellulose chemically. To accomplish this, however, it is necessary to protect the cellulose solution from light and oxygen [5]. Cuprammonium hydroxide, also known as Schweitzer's reagent, is an ammoniacal solution of copper hydroxide. It is prepared by bubbling air through a mixture of copper and ammonium hydroxide. It may be used to a limited extent in the production of regenerated cellulose fibers and widely in analysis as a solvent for cellulose. The degree of polymerization (DP) of cellulose is related to the viscosity of a solution of the cellulose in cuprammonium hydroxide. The viscosity of the solution increases as the DP of the dissolved cellulose increases.

A few crosslinks increase the molecular size of cellulose tremendously and at the same time convert cellulose into a space polymer. Because of the molecular size alone, crosslinked cellulose would be much less soluble in cuprammonium hydroxide than native cellulose. Cellulose dissolves in cuprammonium by first becoming solvated and swollen; then the chains are separated and dispersed. If these chains are crosslinked, they can swell in cuprammonium hydroxide, but the separation of the chains is restricted. A general property of space polymers or crosslinked polymers containing only relatively few crosslinks is that they are essentially insoluble in all solvents. Since certain crosslinked cellulose derivatives are known to be insoluble in cuprammonium hydroxide [1, 4], insolubility in this reagent is suggested as a criterion for detecting crosslinks in cotton cellulose. The method is very simple: if the cellulose does not dissolve in cuprammonium hydroxide it is crosslinked, and if it does dissolve it is not crosslinked, except in cases where alkali-sensitive crosslinks are involved.

[1] One of the laboratories of the Southern Utilization Research Branch, Agricultural Research Service, U. S. Department of Agriculture.

Method

For the purpose of this study, cellulosic samples were analyzed by the cuprammonium-fluidity method described by Conrad [2]. A finely ground sample was extracted for 6 hr with 95% ethanol, shaken in cuprammonium hydroxide containing about 30 g of copper and 165 g of ammonia per liter of solution for 17 hr as in fluidity determinations, to dissolve the cellulose. If all the cellulose in a chemically modified cotton dissolved when carried through the procedure, the fluidity was determined in the usual fashion. If, however, part of the cellulose failed to dissolve, no attempt was made to obtain fluidity values. The appearance of granules in the ammoniacal solution, after the cellulose had been shaken in it for 17 hr, was interpreted as partial insolubility and an indication of crosslinked cellulose. The presence of granules, insoluble cellulosic particles, was easily detected visually. The long extraction period with ethanol may be omitted if the chemically modified cotton has been given a pretreatment to remove waxes and other foreign materials before chemical modification.

It must be recognized that solubility in cuprammonium hydroxide as a method of detecting crosslinks in cotton cellulose has its limitations. Cellulose crosslinked by bonds that are subject to hydrolysis or saponification, such as the ester linkage, is likely to dissolve.

Insolubility of Crosslinked Cotton

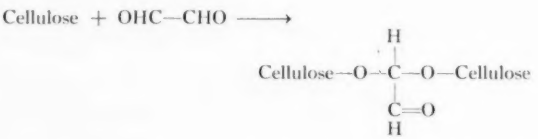
Cotton Insolubilized with Aldehydes

In 1929, it was suggested that cellulose may be crosslinked with formaldehyde [12], and today it is generally accepted that cellulose chains are crosslinked with formaldehyde by the formation of methylene-ether bridges, e.g.,

$$\text{Cellulose} + \text{HCHO} \longrightarrow \text{Cellulose—O—CH}_2\text{—O—Cellulose}$$

The treatment of viscose with formaldehyde reduces swelling in water and therefore reduces the amount of water that can be absorbed or imbibed. Formaldehyde-treated cotton is insoluble in cuprammonium hydroxide [6, 7, 22]. The treatment of cotton yarn with formaldehyde in acidic media produces a chemically modified cotton that resists dyeing with direct cotton dyes, that has a decreased swelling capacity in water, that resists biological rotting, and that is brittle. The resistance to swelling in water in combination with the resistance to direct cotton dyes has been interpreted as evidence of crosslinking [6]. The embrittlement of cotton can probably be expected with many other short-chain crosslinking molecules. Mark, in a general statement concerning the crosslinking of resins of a semicrystalline fiber-form type, said it is not possible to use short-chain crosslinkers without risking brittleness and exaggerated rigidity [11].

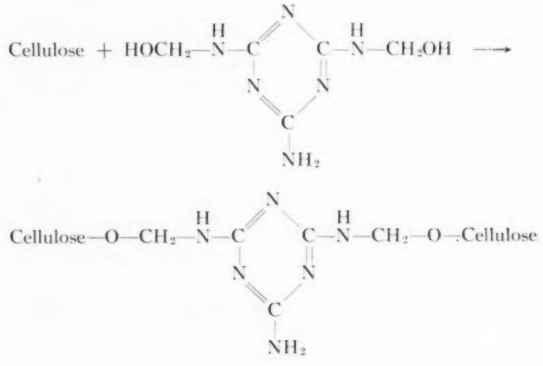
Other aldehydes have also been reacted with cellulose. For example, glyoxal and α-hydroxyadipaldehyde are sold commercially as shrinkage-control agents for cotton. These aldehydes apparently crosslink cellulose chains in cotton. The exact type of bridge formed with glyoxal is not known, but it has been suggested that the bridge contains a carbonyl group, e.g.,



Near ultraviolet absorption data agree with this type of structure, and the reaction product is insoluble in cuprammonium hydroxide.

Cotton Crosslinked with N-Methylol Compounds.

The aminoplast resins which contain N-methylol groups react with cellulose in much the same fashion as formaldehyde. If one considers aqueous formaldehyde to be methylene glycol, then the similarity of the condensation reaction can be seen easily. In each case the methylol groups are attached to electronegative atoms. The reactions of a methylolmelamine with cellulose may be indicated as follows:

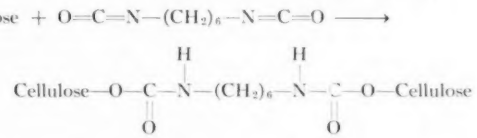


It might be pointed out that the extent of this reaction is no doubt small as compared to the reaction leading to resin formation. Cotton treated with the aminoplast resins is insoluble in cuprammonium hydroxide [4].

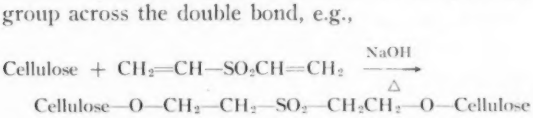
Of all the properties contributed to cotton by crosslinking agents, shrinkage control is of greatest economic importance at present. All of the known shrinkage-control agents for cotton that are used commercially are either known crosslinkers or are potential crosslinkers. These include formaldehyde, glyoxal, α-hydroxyadipaldehyde, and numerous trade products which are N-methylol products, that is, urea formaldehyde- and melamine formaldehyde-type materials.

Cotton Crosslinked with Diisocyanates and Vinyl Sulfone

Other compounds that are known to crosslink cellulose are the diisocyanates and vinyl sulfone. These agents also contribute shrinkage resistance to cotton. Hexamethylene diisocyanate has received some attention in England recently as a textile finishing agent [21]. Cellulose treated with this reagent is insoluble in cuprammonium hydroxide [10]. Its reaction is typical alcohol-isocyanate addition, e.g.,



There is very little doubt that vinyl sulfone crosslinks cotton. It forms polymers with glycols in the presence of basic catalyst [16]; starches and dextrins are made insoluble in boiling water by treatment with vinyl sulfone [17]; and, when cotton is treated with vinyl sulfone in the presence of basic catalyst, the cotton is made shrink resistant [18] and insoluble in cuprammonium hydroxide [19]. This reaction proceeds by the addition of a hydroxyl group across the double bond, e.g.,



Cotton Crosslinked with Two-Carbon-Chain Crosslinks

In order to demonstrate that insolubility in cuprammonium hydroxide is associated with crosslinking and not with the nature of the chain of the reacted group, a number of compounds containing a two-carbon group, similar except that some were crosslinkers and some were not, were reacted with cotton, which was then subjected to cuprammonium hydroxide. For example, aminoethyl cellulose was made by heating 2-aminoethyl sulfuric acid with cellulose in the presence of strong alkali solutions [8, 13]. This cellulosic derivative was soluble in cuprammonium hydroxide according to the Conrad method. If the degree of substitution was high enough (about 1.4% nitrogen or greater), it would dissolve in dilute alkali and in dilute acetic acid. The cuprammonium fluidity of aminized cotton (aminoethyl cellulose) containing about 0.3 to 1.0% nitrogen ranged from about 8 to 20 rhes, indicating some degradation during treatment. The fluidity varied somewhat according to the severity of the heat treatment, but in all cases the aminized cotton was soluble in cuprammonium hydroxide. A print cloth containing 0.67% amino nitrogen, prepared from 30% sodium hydroxide and 20% 2-aminoethyl sulfuric acid by the alkali-heat-cure method, had a fluidity of 15.4 rhes. The term "alkali-heat-cure method" is used herein to describe a process which includes the moistening of cotton with a solution containing about 20 or 25% sodium hydroxide and some reagent that may be reactive toward cellulose, and heating the impregnated cellulose for about 15 to 30 min at about 110°C.

Halogen esters of alkyl compounds, such as chloro- and bromoalkyl compounds, react with cellulose in the presence of alkali in much the same way as do the sulfuric acid esters. This was demonstrated a number of years ago by Hartman [9]. These halogen esters tend to be much less soluble in strong alkali solutions than the sulfuric acid esters and are therefore less satisfactory for reaction in alkaline media.

Alkyl sulfonic acids do not react with cotton in the presence of alkali; 2-aminoethyl sulfonic acid was applied to cotton by the alkali-heat-cure method, but the cellulose was not modified other than by the effects of the strong alkali. The treatment did not introduce any nitrogen into the cellulose. Now, with the knowledge that a haloalkyl compound reacts with cellulose and that sulfonic acid esters of an alkyl compound do not, let us consider the reaction of a compound that contains both chloro and sulfonic acid ester groups. Various amounts of chloroethylsulfonic acid were dissolved in 25% sodium hydroxide solu-

tion and applied to print cloth by the alkali-heat-cure method. This reagent modified the cellulose. Up to about 1.8% sulfur was introduced. Sufficient sulfonic acid groups were introduced to impart an ion-exchange capacity of about 675 meq/kg of modified cotton. The formation of sulfoethyl cellulose may be represented as follows:

$$\text{Cellulose} + \text{Cl}{-}\text{CH}_2\text{CH}_2{-}\text{SO}_3\text{H} \longrightarrow \text{Cellulose}{-}\text{O}{-}\text{CH}_2{-}\text{CH}_2{-}\text{SO}_3\text{H}$$

This sulfoethyl cellulose, even with relatively large amounts of sulfur, is soluble in cuprammonium hydroxide. Fluidity values were in the range of 5 rhes, which is about the range found for native cotton.

According to the above facts, an alkyl compound containing both the sulfato and halo groups should crosslink cellulose when it is dissolved in a strong sodium hydroxide solution and applied to cotton by the alkali-heat-cure method. In order to obtain a compound of this nature and at the same time one closely related to the above compound, fuming sulfuric acid was reacted with ethylene chlorohydrin to form chloroethylsulfuric acid by a modification of the Suter and Oberg method [20]. An aqueous solution containing 10% chloroethylsulfuric acid and 25% sodium hydroxide was applied to print cloth according to the alkali-heat-cure method. The treated fabric contained 0.38% sulfur and 0.10% chlorine. This fabric was relatively insoluble in cuprammonium hydroxide; about 25 to 50% failed to go into solution. The insoluble portion appeared as small granules and could easily be detected. In another experiment, fabric was treated three times with the chloroethylsulfuric acid solution already described. It also failed to dissolve completely in cuprammonium hydroxide. This fabric contained 0.32% sulfur and 0.03% chlorine. The presence of small amounts of chlorine and sulfur in the cellulose indicated that some of the chloroethylsulfuric acid molecules only reacted at one end. In all probability a large percentage of the chloroethylsulfuric acid molecules reacted at both ends to crosslink cellulose molecules. The reaction can be illustrated as follows:

$$\text{Cellulose} + \text{Cl}{-}\text{CH}_2\text{CH}_2{-}\text{OSO}_3\text{H} \xrightarrow[\Delta]{\text{NaOH}} \text{Cellulose}{-}\text{O}{-}\text{CH}_2\text{CH}_2{-}\text{O}{-}\text{Cellulose}$$

Three-Carbon-Chain Crosslink

Now let us consider some longer chain molecules which react with cellulose. 3-Sulfatopropylamine was dissolved in 20% sodium hydroxide and applied to print cloth by the alkali-heat-cure method. About 0.4% nitrogen was introduced. The aminopropyl cellulose dissolved in cuprammonium hydroxide to give a fluidity value of about 15 rhes.

Next, print cloth was treated with α,γ-glyceroldibromohydrin in the presence of alkali. Since the bromohydrin was relatively insoluble in sodium hydroxide solutions, a two-step process was used: cloth was first moistened with 25% sodium hydroxide and then the bromohydrin was padded onto the wet "alkali cellulose." After 19 hr at room temperature, the fabric was thoroughly washed and then found to be insoluble in cuprammonium hydroxide. The reaction can be represented by indicating a propanol crosslink, e.g.,

$$\text{Cellulose} + \text{Br}{-}\text{CH}_2\text{CH(OH)CH}_2{-}\text{Br} \longrightarrow \text{Cellulose}{-}\text{O}{-}\text{CH}_2{-}\text{CH(OH)CH}_2{-}\text{O}{-}\text{Cellulose}$$

A mixture of 75% α,β- and 25% α,γ-glycerol dichlorohydrin reacted with cotton under the conditions described above for the bromohydrin. This cotton was also insoluble in cuprammonium hydroxide.

Four-Carbon-Chain Crosslink

1,4-Disulfato-2-butyne was made by sulfating the corresponding diol with pyridine chlorosulfonic acid. It was isolated as the disodium salt. Cotton cellulose was treated with an aqueous solution containing 10% of the disodium salt of 1,4-disulfato-2-butyne and 20% sodium hydroxide according to the alkali-heat-cure method. This treatment did not cause any visual changes that did not accompany an alkali treatment alone. The cotton did not contain sulfur or other elements that could be attributed to the reaction. It would not dye readily with methylene blue dye, which also indicates the absence of sulfato groups. Up to this point no positive evidence of reaction was obtained, but when a piece of the fabric was placed in bromine water it absorbed bromine; this was good evidence of reaction. Also, when some of the butyne-treated and alkali-treated control cotton was dyed in a differential dye bath, indication of reaction was obtained. 1,4-Disulfato-2-butyne-treated fabric dyed yellow and alkali-treated control fabric dyed blue. The differential dye bath contained Pontamine Fast Blue (a direct cotton dye) and Celliton Fast Yellow RRA (an acetate dye). This combination of dyes has been used to indicate the degree of substitution and uniformity of partially acetylated cotton [3]. Unacetylated cotton dyes blue, while acetylated cotton dyes yellow. In the case of the butyne-crosslinked cotton the lack of affinity for the direct cotton dye and the affinity for the ace-

tate dye are probably related to the number of the hydroxyl groups in the cellulose that have been blocked, and are not related to the nature of the substituted group. The reaction can be illustrated as follows:

$$\text{Cellulose} + HO_2SO{-}CH_2{-}C{\equiv}C{-}CH_2{-}O{-}SO_3H \xrightarrow[\Delta]{NaOH} \text{Cellulose}{-}O{-}CH_2{-}C{\equiv}C{-}CH_2{-}O{-}\text{Cellulose}$$

This product did not dissolve completely in cuprammonium hydroxide solution.

Crosslinking of Cellulose with Potassium (Disulfatoethyl) Amine

Potassium (disulfatoethyl) amine made by sulfating diethanolamine with chlorosulfonic acid [14] is very soluble in strong sodium hydroxide solution and reacts with cotton in the alkali-heat-cure method. It did not react with cotton to the extent that 2-aminoethyl sulfuric acid did; only about 0.3% nitrogen was introduced by a 25% alkali solution containing 7% of the disulfatoethyl amine when it was reacted with print cloth in the alkali-heat-cure method. About 0.4% nitrogen was introduced when the alkali solution contained 20% of the amine. Both ends of the molecule are capable of reacting with cellulose, e.g.,

$$\text{Cellulose} + HO_2SO{-}CH_2CH_2{-}NH{-}CH_2CH_2{-}OSO_3H \xrightarrow[\Delta]{NaOH} \text{Cellulose}{-}O{-}CH_2CH_2{-}NH{-}CH_2CH_2{-}O{-}\text{Cellulose}$$

The crosslinked cellulose was partially insoluble in cuprammonium hydroxide. Cellulose crosslinked with a chain containing 5 atoms should be somewhat less brittle than cellulose crosslinked with chains containing 1 or 2 atoms.

Crosslinking of Cellulose with THPC

In the work on making cotton flame resistant with THPC resin [15] the question has been asked, "Is the resin in actual chemical union with the cellulose or is it merely held mechanically?" In order to answer this question, it was decided to see if THPC itself would react with cellulose [THPC is an abbreviation used to represent the compound tetrakis(hydroxymethyl)phosphonium chloride.] A 10% aqueous solution of the crystalline compound was used to moisten cotton print cloth. The moistened fabric was heated for 5 min at 140°C, then washed thoroughly in hot and in cold water and air dried. The fabric contained 0.6% phosphorus, which represents about 1 phosphorus atom per 17 anhydroglucose units. The reaction can be represented as a condensation between methylol groups and cellulosic hydroxyls, e.g.,

$$\text{Cellulose} + (HOCH_2)_4PCl \xrightarrow[\Delta]{} \text{Cellulose}{-}O{-}CH_2{-}\underset{\displaystyle O}{\overset{\displaystyle \|}{P}}(CH_2{-}O{-}\text{Cellulose})(CH_2{-}O{-}H)$$

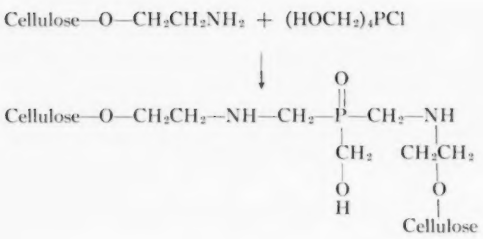
The cellulose was crosslinked and partially insoluble in cuprammonium hydroxide. In the above equation, the phosphonium structure was converted to a phosphine oxide because phosphonium compounds in general are converted to phosphine oxides by heat. During the conversion hydrochloric acid, formaldehyde and hydrogen were released.

Crosslinking of Aminized Cotton with Formaldehyde and THPC

It has already been pointed out that aminized cotton, 2-aminoethyl cellulose, is soluble in cuprammonium hydroxide. It can be made insoluble, however, by crosslinking it with formaldehyde or with THPC through the amino groups. These amino groups are reactive primary amines and like other amines they condense with formaldehyde or with THPC under very mild conditions. By exposing aminized fabric to vapor of formaldehyde for 2 hr at 110°C, it was made insoluble in cuprammonium hydroxide. This reaction may be represented as follows:

$$\text{Cellulose}{-}O{-}CH_2CH_2NH_2 + HCHO \longrightarrow \text{Cellulose}{-}O{-}CH_2{-}CH_2{-}NH{-}CH_2{-}NH{-}CH_2CH_2{-}O{-}\text{Cellulose}$$

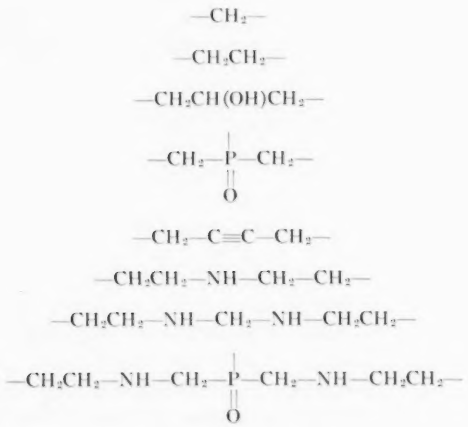
Aminized cotton containing 0.7% nitrogen was crosslinked with THPC by moistening the fabric with a dilute aqueous solution of the phosphorus compound and then heating it at 110°C for about 10 min. The treatment introduced 1.0% phosphorus and made the fabric insoluble in cuprammonium hydroxide. In this reaction the methylol groups of THPC condensed with the amino groups, e.g.,



Summary

The results of this investigation show that cotton cellulose crosslinked even with relatively few links containing amine, ether, or phosphine oxide groups is partially insoluble in cuprammonium hydroxide. The insoluble part appears as granules and can easily be detected. Insolubility provides a convenient and easy method of detecting alkali-stable crosslinks in cotton. If a modified cotton dissolves in cuprammonium hydroxide, it is not crosslinked; if it does not dissolve, it is crosslinked.

Cellulose was treated with a number of compounds, some of which were monofunctional in respect to reactivity with cellulose and some were polyfunctional. In all cases where the compounds could react with cellulose at one end only, the product was soluble in cuprammonium hydroxide. The products were insoluble in every case where the compound could theoretically crosslink the cellulose chains. The cotton was crosslinked with links ranging from 1 to 9 atoms in the links, e.g.,



Acknowledgment

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Special Elastic Properties of Cotton Yarn and Cloth Mercerized without Tension

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Abstract

Suitable cotton yarn or cloth mercerized without tension shrinks and its elastic properties are changed. Either yarn or fabric in its "shrunk" form shows greater than normal elongation, approximately in accordance with the amount of shrinkage that it has undergone. Either, also, tends to have increased elasticity. This feature is especially notable at low loads in open-weave fabrics, which usually have considerable stretchability after shrinking. Such elasticity is illustrated by a semielastic and conforming cotton gauze bandage which is in successful commercial production. This type of shrunk material, in heavier goods, appears adaptable to other uses, such as base fabrics for coating when elasticity is a required property of the coated fabric.

Introduction

The possibility of employing mercerization without tension, i.e., slack mercerizing, to change the elastic properties of cotton yarns and fabrics, and to bring out other unusual properties in cotton, has aroused interest for many years. However, relatively little application of this principle has been made to products for various end uses that have been proposed. Hence the possible wider utilization of the changed properties of cotton in various forms, imparted by slack mercerizing, has been of interest at the Southern Regional Research Laboratory ever since the beginning of its work on the chemical treatment of cotton.

The first slack mercerizing was by John Mercer in 1844, when he was working on a theory of solution. Upon filtering strong sodium hydroxide solution through cotton cloth he observed that the cloth became shrunk and puckered. Mercer, being a textile man as well as a chemist, noted that he had obtained something new with somewhat the effect of the fulling of woolen cloth. The "fulled" cotton might have aroused more interest, but there was no commercial caustic soda at that time.

Although Mercer noted several of the important effects of mercerizing on cotton, he apparently did not notice whether he had changed the elastic properties of his cloth. His discovery was regarded as an invention and patented in 1850 [2]. Even when commercial caustic became available, his process was not utilized because added cost due to the shrinkage was considered too great. There have been attempts ever since the time of Mercer to utilize slack mercerizing, and a number of patents have been issued for special effects.

A successful process in this class is that for producing fabric for suede gloves by knitting from cotton yarn, consolidating the fabric by shrinkage in caustic soda, and napping by slightly raising the surface fibers. The gloves have the usual conforming properties of knitted goods and no doubt benefit also from improved elastic properties due to the shrinkage of the cloth.

Slack-, or shrunk-, mercerized fabrics appear to have been suggested principally for properties other than improved elasticity. According to some patents a wool-like character may be imparted to cotton. If actually obtained, however, the wool effect is due in part to improved elastic properties of the cotton fibers—an increased resiliency or loftiness which, with a slight harshness, must be largely responsible for any wool effect.

Caustic crepes or plissé styles are examples of shrink mercerizing in local areas or stripes, by the aid of printing. These styles have been produced in large quantities, but their value lies more in the over-all effect than in the elastic properties of the mercerized portions.

[1] One of the laboratories of the Southern Utilization Research Branch, Agricultural Research Service, U. S. Department of Agriculture.

Yarn has occasionally been allowed to shrink in commercial mercerizing to enhance its dyeing capacity. Samples examined had apparently been shrunk in a warp mercerizing machine so that they were finished at about 10% below the original length of the yarn, and had been made more coarse by a similar amount. Such yarn should have somewhat greater elongation and elastic recovery than usual at low loads, but any advantage in knitting was apparently considered secondary to the effect on dyeing.

TABLE I. Effect of Shrinkage of Fabrics by Slack Mercerization *

Description of Fabrics		Thread Count, Warp and Filling	Shrinkage		Elongation at Break	
			Warp (%)	Filling (%)	Warp (%)	Filling (%)
1 Bleached gauze	Before	44×36	—	—		
	After	63×55	35	33		
3 Bleached gauze	Before	28×24	—	—		
	After	46×40	42	42		
5 Bleached gauze	Before	20×12	—	—		
	After	33×23	47	45		
7 Twill	Before	121×52	—	—	10.7	9.1
	After	156×80	35	24	74.7	34.0
9 Plain weave	Before	79×40	—	—	13.3	8.8
	After	102×57	29	24	64.8	38.3
11 Print cloth	Before	64×60	—	—	12.4	16.9
	After	85×79	26	25	48.9	52.5
13 Osnaburg (light)	Before	28×25	—	—	12.9	22.9
	After	39×36	28	30	52.3	67.2
15 Bagging (heavy)	Before	20×21	—	—	20.3	24.9
	After	28×28	25	30	51.4	69.9

* The cloth was as free as possible to shrink in caustic soda, usually of 22–23% concentration.

Representative of the direct shrinking of cotton fibers is a nonwoven fabric. According to the patent [9], it is made made without a binding agent, by allowing full shrinkage of fibers in a web which decreases greatly in area as the fibers twist and bend, and tend to interlock and felt, as they shrink.

An example of a woven fabric with new elastic properties imparted by mercerization is a type of cotton gauze bandage [3, 4, 5, 11] developed at the Southern Regional Research Laboratory, now in production for the Armed Services Medical Procurement Agency. It has been described as semielastic and body conforming; and it was made initially from various types of gauze, shunk as much as possible in caustic soda of 22 to 30% concentration, and washed and dried with a minimum of tension. Production is in commercial hands, and several millions of the bandages have been made. While the surface texture is important, the use of the bandage depends greatly upon the elastic properties imparted by slack mercerizing.

There have been a good many other patents in this general field, a number of them claiming effects of differential shrinkage brought about by the shrinkage of cotton when combined with other fibers, or with treated cottons which shrink less than cotton itself.

TABLE II. Supplementary Data for Fabrics of Table I

Number of Fabric	Yarn Number		Twist		Weight per Sq Yd (oz)	Area Remaining (%)
	Warp	Filling	Warp (t.p.i.)	Filling (t.p.i.)		
1	29.4	37.6	21.3	23.1	1.4	—
2	—	—	—	—	3.4	43.6
3	30.7	43.2	20.5	22.4	.94	—
4	—	—	—	—	3.00	33.6
5	33.0	40.5	19.8	23.6	.63	—
6	—	—	—	—	2.25	29.2
7	36.3	40.4	17.1	21.7	3.25	—
8	—	—	—	—	5.8	49.4
9	36.6	20.2	22.0	15.3	3.05	—
10	—	—	—	—	5.25	54.0
11	27.8	40.0	16.7	26.8	2.75	—
12	—	—	—	—	4.45	55.0
13	9.5	11.55	13.7	14.1	4.1	—
14	—	—	—	—	7.35	50.4
15	4.5	4.15	8.6	9.5	7.4	—
16	—	—	—	—	13.4	52.5

Basis of the New Elastic Properties

The basis of increased stretchability and other changes in elastic properties of slack-mercerized cotton materials may seem to be shrinkage, but it is really swelling. Swelling of their fibers causes cotton materials, whether fiber, yarn, or knitted or woven fabrics, to tend to shrink in strong sodium hydroxide solutions, although there is relatively little effect with heavy or tight structures like cords and many ducks.

Shrinkage of Cotton Fibers

The shortening of cotton fibers when free to shrink in sodium hydroxide has usually been reported as 15 to 19% at concentrations which are considered to be of mercerizing strength. As will be pointed out, such figures are not at all a measure of what takes place in yarns and fabrics. Although the percentage shrinkages of the latter may be of the same order, it is frequently considerably greater.

Shrinkage of Yarn

The free shrinkage of cotton yarn in sodium hydroxide depends upon the structure and twist of the yarn, and upon other conditions, as well as the usual variables of sodium hydroxide solutions. Recorded results have shown differences in yarn shrinkage with time, temperature, and concentration at the time of treatment, from roughly 19 to 23%. As a specific example of somewhat greater shrinkage, a carded singles yarn [12/1 of twist multiplier (T.M.) 3.5] in loose open skeins under most favorable conditions shrunk about 33% in caustic soda solution at room temperature. The skeins were measured under a moderate tension after washing and drying with as little handling as possible. In contrast, similar skeins from the same lot of yarn shrunk only about 26% while hanging loosely on a roller under barely enough tension to allow the yarn to turn in the caustic. Thus there was a considerable effect from relatively little restraint; shrinkage may be greatly restrained even by the relatively light load alone, of the weight of the caustic soda solution carried by the swollen yarn. It will be obvious that reports of such shrinkages are not very significant unless various details are given.

Experience with plied yarns indicates that they may tend to shrink less than singles; 40/2 yarns with T.M.'s of 3 shrunk to maxima of 22–25%.

Shrinkage of Fabrics

Here again, the shrinkage depends upon structure, that of the constituent yarns as well as of the fabric; upon conditions of treatment; and upon the usual variables of the treating solution. A few examples of shrinkages are shown in Tables I and II. Table I shows the comparative shrinkages of fabrics of different constructions, with the resulting thread counts, and elongations at break before and after shrinking. Table II merely adds more data for the same fabrics. It shows initial yarn numbers and twists, the old and new weights per square yard, and percentages of cloth area remaining.

Shrinkage may vary from 10 or 15% (Table V) to nearly 50% (Table I), and tends to increase with openness of structure. Percentage losses in area may be much greater; for 10% shrinkage in each direction there would be a loss of area of 19%, and for 40% shrinkage each way a loss of 64%. That is, in the last case, little more than a third of the area remains (Table II). Although the shrinkage does not result in the loss of any cotton, it offers difficulties. For example, it may not always be convenient to use the wide looms required so that a fabric of usable width will result after shrinking.

Causes and Nature of Shrinkage

The shrinkages of yarn and fabric undoubtedly result far more from the great lateral swelling of the cotton fibers than from their shrinkage in length. In spite of a possible great effect on shrinkage from relatively little restraint, swelling can be very forceful, as brought out in studies of the tensions developed in yarns during mercerizing [7, 8]. Yarn not only expands in diameter with its constituent fibers, but the fibers swell also, in a sense, against the twist. Since the outside fibers need to be longer instead of shorter, to spiral around a singles yarns at its new and greater diameter, an adjustment takes place as the fibers increase their twist angles at the expense of yarn length.

Figure 1 represents, in a greatly oversimplified way, changes in a singles yarn as it shrinks by 25% in length. The volume is assumed to remain unchanged, because so much of the swelling of the fibers is taken up in the normal air spaces between them that there is no definite basis for the estimation of any additional volume. Hence the diagram represents more nearly the state of the yarn after washing and drying than while swollen. The shrunk yarn should, no doubt, appear somewhat more bulky because there are larger air spaces between fibers. For practical purposes, the actual volume of dry fiber substance is unchanged by the shrinking process, because mercerized cellulose is only about 1% less dense than native cellulose. Since the volume is assumed to remain the same, one-fourth of the yarn is shown as shrunk into the length of the re-

maining three-fourths. The figure represents side views of the yarn before and after slack mercerizing, with closing up of twist and change of twist angle.

Test pieces of equal lengths of the yarns before and after treatment are obviously quite different (Figure 1), the mercerized containing much more cotton and more turns per inch. More turns, greater twist angle, and more interspace for the fibers to move in all contribute to greater elongation of this very different test piece.

In fabrics there are the same swelling forces and tendencies in the constituent fibers and yarns, with the added complication of crimp. As yarns expand in diameter, in both warp and filling, greater lengths are necessary to go over and under them in the cloth structure. An adjustment must take place, and, if the cloth is free to shrink, the members of each set of threads, ends and picks, are drawn closer together by the other set, and the swelling takes place at the expense of length and width of the fabric. A closely woven piece may change but little; one that is more open will close up; while in a very open fabric there may be visible yarn as well as cloth effects. For example, in an open gauze structure there is much opportunity for yarn movement, and the swelling may actually distort the yarn into kinks. A change of this nature is shown in Figure 2, in photographs of 28 × 24 gauze, and of a bandage fabric made from it with shrinkage of about 35 by 40%. Most of the bandages made later at the Southern Laboratory were from the much more open 20 × 12 gauge.

A diagram (Figure 3) may allow easier visualization of what happens during the slack mercerization of cloth. It represents approximately the effects with the light Osnaburg, No. 13 and 14 of Tables I and II, which is to be discussed later. Test pieces of equal size cut from areas of shrunk and unshrunk fabric will be very different in properties, as will be shown below. The possibilities for drastic changes in cotton textiles by swelling are indicated by Willows and Alexander [12] and by Coward and Spencer [1], who determined by different methods that the volumes of Egyptian cotton fibers swollen in sodium hydroxide were 3.6 and 3.8 times that of the volumes unswollen. Coward and Spencer, who employed a centrifuge method, found also that bleached cloth, 93 × 104, made from Egyptian cotton, swelled to 2.6 times its original volume as compared with the 3.8 above for fiber, in spite of the restrictions imposed by yarn twist and weave (both values were calculated by the present authors from the original data). No such figure is very definite, but it is clear that there is opportunity for great changes in fiber and fabric.

The discussions above suggest an error that is sometimes made in reporting elongations of chemically modified cotton yarns and fabrics. Increased elongation should only be claimed as due to action of reagents on the cotton cellulose after allowance has been made for any contribution, sometimes relatively great, from shrinkage of the yarn or cloth incident to the treatment in question.

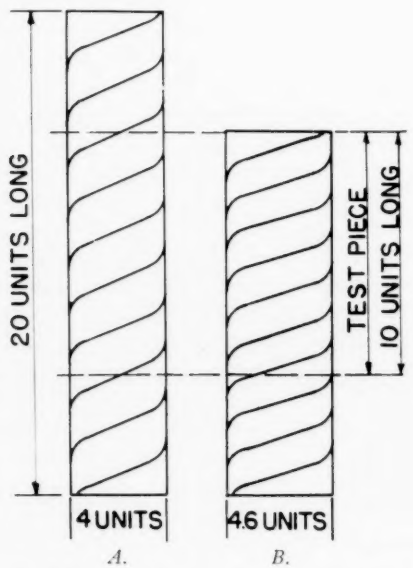

Fig. 1. Diagrams of yarns before and after shrinking. Swelling of the fibers in a short length of singles yarn (*A*) results in change of twist angle and decrease of length (*B*).

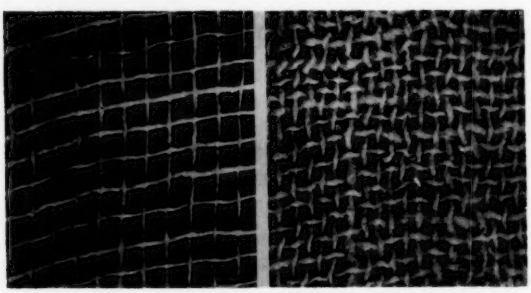

Fig. 2. Example of slack mercerization. Gauze, 28 × 24, shown before and after mercerizing with shrinkage, to make a bandage fabric with many crimps and kinks.

The New Elastic and Related Properties

Stretchy yarns or fabrics are particularly difficult to work with in the test laboratory, because there is no satisfactory way to measure samples initially. For convenience, a simple ruler test of sufficient accuracy for measuring stretch and elastic return of bandage fabrics was adopted. A strip of the bandage was simply laid along a ruler, held suitably at its ends, stretched by a predetermined percentage, allowed to return freely, and measured again to determine the amount of recovery. This rough test for bandage, which can be employed with other stretchy fabrics, has the advantage that it avoids complications such as the necessity for determining equivalent initial loads or tensions for measuring comparatively samples of different weights and elastic properties.

Yarns

The yarns already described, shrunk from a 12/1 of 3.5 T.M. (12 t.p.i.), to two different degrees, are shown with the original in photographs in Figure 4. The one with the extreme shrinkage is probably too crimped and kinked for almost any use, but it shows what yarn tends to do. It was greatly straightened under a moderate measuring tension and showed a shrinkage of only 32%. On the other hand, No. 2, with 26% shrinkage, is not obviously very stretchy. The elastic properties are partly indicated by the load-elongation curves in Figure 5, reproduced from tests on skeins of the yarns just described. Owing to uncompensated differences in the yarns, this is only a qualitative picture, but it shows how greatly yarn can be changed in stretchability by mercerizing without tension. The most noticeable elongation is that of crimps and bends (Figure 4, No. 3) and, no doubt, of opening and closing of yarn structure. Yarn of this last type might serve as a basis for highly and durably elastic

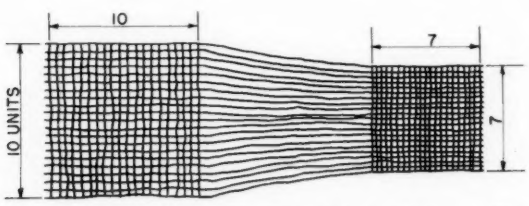

Fig. 3. Diagram to show effects of cloth shrinkage. The cloth is represented as having shrunk 30% in each direction. The new area is 49% of the old.

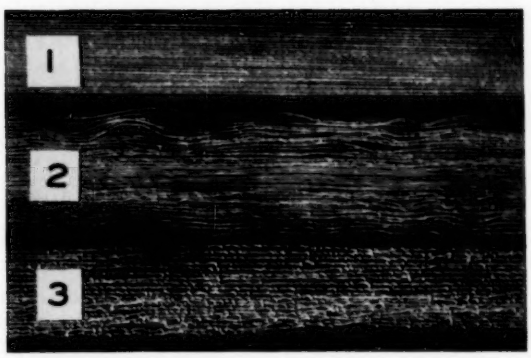

Fig. 4. Singles yarn before and after slack mercerizing. 1, Before; 2, shrunk with some restraint; 3, shrunk as freely as possible.

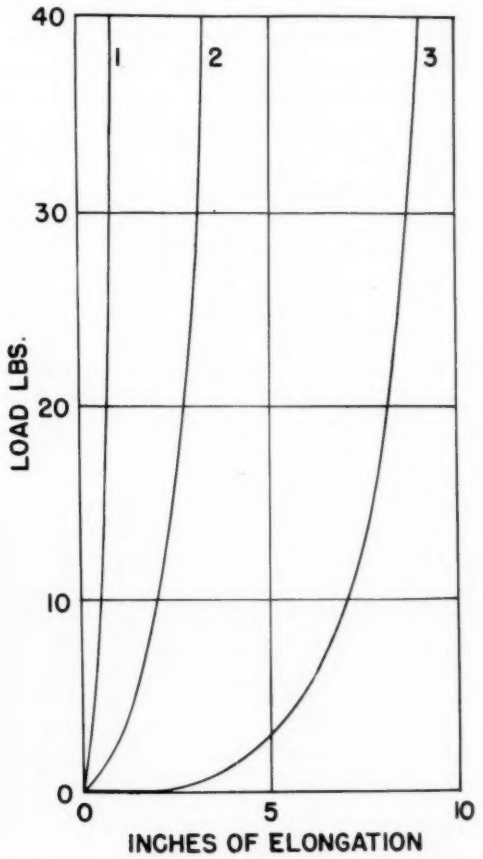

Fig. 5. Load-elongation curves of singles yarns of Fig. 4. 1, Before; 2, shrunk with some restraint; 3, shrunk as freely as possible. (Reproduced from Instron curves.)

cotton yarn if a way could be found to fix it suitably in the crimped and kinked form. Until rendered more durable, shrinkage and stretchability of yarns will be found somewhat difficult to retain and utilize.

In contrast to the usual desire to retain stretchability, advantage was taken of the tendency to lose it, in attempts to make an improved cotton tire cord [6]. Although changes in textile economics caused this development to be abandoned, it may be of interest for some other application of shrunk yarns. Singles yarns (usually 12/1) were shrunk about 15%, allowed to return in length about 5% during washing, then plied and made into tire cord. By the time the cord was finished the loss of length was nearly all recovered and there was no need for any notable adjustment in original yarn number to meet tire-cord specifications. The properties being sought, increased heat resistance and hot flex resistance, were retained in the cord as far as could be judged by laboratory tests.

Fabrics

The elastic properties of the fabrics are shown by suitable load-elongation curves; and until the Instron machine became available some of the most instructive were derived from direct loading with small weights. A typical curve for a bandage fabric is shown in Figure 6*A*. The stretch and recovery follow different courses—the stretch to about 20%, the usual basis for routine tests of the bandage, and the recovery to a residual stretch of about 4–5%. The curve plotted during an ordinary breaking test on a pendulum-type machine is reproduced in Figure 6*B*; the unusually long vertical part of this curve is due mainly to inertia in the system. The curve derived from manual loading represents more nearly what actually happened within the vertical part of the other curve.

The lower curve in Figure 6*B* was reproduced from an equivalent breaking test in the warp direction of a sample of the same number of threads from the original fabric. Such curves, for fabrics before and after shrinking, indicate the great changes in elastic properties but are not strictly comparable because of the great change in the size and unit weight of the cloth. While the vertical part of the pendulum-machine curve really represents error, it may give an indication of the approximate amount of easy stretchability of slack-mercerized samples.

It can be seen by comparison of Figures 6*A* and 7*C* that, in the absence of special equipment, useful results can be obtained by simple manual loading.

Heavier fabrics behave much the same. Number 13 in Tables I and II was an open-weave Osnaburg, the only fabric immediately available, of about the same thread count as the gauze just discussed, but heavier. It shrunk about 30% in the filling and about 28% in the warp. Test pieces in the warp direction yielded the curves reproduced in Figure 7. The curve in *A* is that of a pendulum-type machine and is similar in general form to one that has already been discussed. The curve in *B* is from an inclined-plane machine and, as usual, has the axes reversed with reference to *A*; it shows much easy stretch but is seriously affected by inertia in the region of its principal change of direction. The curve in *C* is from an Instron machine [2] and is of much the same type as obtained from manual loading with light weights. It shows what really happens in the lower portions of the other curves while loading, and also while unloading. There is relatively high elastic

[2] All Instron tests on fabrics, mentioned in this paper, were made at 3-in. gage length on strips 2 in. in width, which were stressed to 1 in. per min.

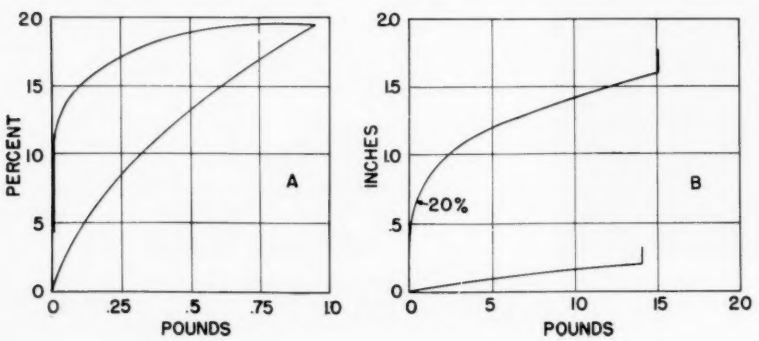

Fig. 6. Load-elongation curves for a conforming gauze bandage fabric. The fabric is original and shrunk, bleached 28 × 24 gauze similar to the fabrics of Figure 2. *A*, curves by manual loading; *B*, curves reproduced from a pendulum machine.

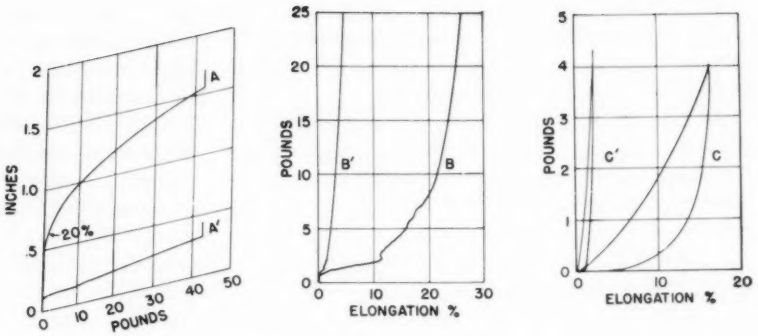

Fig. 7. Load-elongation curves for heavier, open-weave, shrunk and unshrunk fabric. Curves are from: *A*, pendulum, *B*, inclined-plane, *C*, Instron machines. *A'*, *B'*, and *C'* for fabric before shrinking (13 and 14 in Tables I and II).

recovery. Curves marked *A'*, *B'*, and *C'* represent the fabric before it was shrunk by mercerizing, and serve to emphasize the effects of that process.

Relaxation tests were made [10] on several samples of bandage, including some of commercial production, and all believed to have been made from 20×12 gauze. When strained in the Instron machine and held, the stress decay occurred, in general, logarithmically with time. More specifically, when stretched by 20% and held for 1 hr the specimens lost about one-third of their load; when stretched similarly by 40%, they lost nearly one-half their load in 1 hr.

In Figure 8, a 2-in. test strip of the shrunk Osnaburg was loaded on the Instron apparatus to stretch it to somewhat below half its elongation at break and then unloaded to a low value (1½ lb) for cycling. In contrast to the elasticity shown in Figure 7*C*, there was less elastic return from this higher elongation, although the test piece would have recovered more if it had been completely unloaded. Since the recovery curve is practically the same for the first and tenth cycles of loading and unloading, there is true elasticity in this range of elongation. The elasticity here is apparently not much greater than in the original fabric, but there is much greater elongation up to the breaking load. Further tests on relaxation and cycling will, no doubt, be of interest as specific problems in the utilization of slack-mercerized fabrics arise.

A few practical tests on bandage fabrics indicated that stretches of 5 or 10% became unrecoverable if held for any length of time, that is, that bandages rolled too tightly would not perform normally if used immediately after standing in a tight roll. There might be slow recovery, which was not of interest at the time.

The success of the bandage apparently depends greatly upon its ability to stretch to a relatively high degree and to tend to return elastically to near its original length. When applied to the person, it is commonly wound on with some strain so that it exerts mild pressure. While in this position of moderate strain, it can stretch or shrink with the limited movement of a patient, and is capable of doing so over and over again. Suitable heavier slack-mercerized fabrics should serve similarly if there are other situations in which the elastic requirements are similar.

Breaking strengths of cloth seem to be slightly improved by slack mercerizing (Table III) even when tested on samples with equal numbers of threads, that is, without the benefit of the extra threads brought in by the shrinking. This was found true in 7 out of 10 comparisons and may be partly accounted for by changes in the structure of the yarn in the direction being tested, possibly by assistance

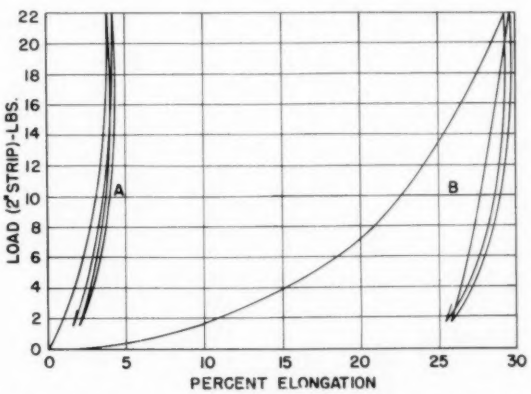

Fig. 8. Cyclic loading of original and shrunk fabric. First and tenth cycles are shown. *A*, Osnaburg; *B*, shrunk (13 and 14 in Tables I and II).

from the larger number of cross threads in the test piece, and possibly by the greater diameter of the shrunken yarns, which seems, in some cases, equivalent to the presence of more cotton.

An estimate of "permanent" shrinkage may be of interest, and can be based on the percentage of shrinkage and the percentage elongation at break as normally determined, through calculation of percentage of "length at break." For a shrunk fabric the latter is the percentage of length remaining plus the corresponding proportion of the elongation at break; for the unshrunk sample it is the length of test piece (100%) plus the percentage elongation at break. Lengths at break and sample calculations are shown with Table III. Of 10 comparisons for the 5 shrunk fabrics covered, 2 show slightly greater lengths at break in the warp but lower in the filling than the original fabrics; all the others showed lower lengths at break in both warp and filling. The losses, which might be regarded as permanent or nonrecoverable shrinkages, ran from 1.5 to 6.7%. The apparent exceptions may quite possibly be due merely to unbalance. Permanent shrinkage is obviously not great in these fabrics.

The observed effects of slack mercerizing suggested possible improvement in tear strength, and two fabrics tested showed practically doubled tear strength in each direction in the trapezoid test (Table IV). The Osnaburg lost half its area and had twice the tear strength, which might seem quite logical except that the effective area at the point of tear is more than half the original area. The result is, therefore, to be interpreted as a net gain, even though fabrics before and after shrinking are not strictly comparable. The 80 × 80 print cloth showed the same relative gain, but in this case the gain in tear strength was relatively much greater than the change in area of the fabric due to shrinking. Prospects for practical utilization of this principle seem best with more closely woven fabrics which will not become too stretchy, or lose too much area upon shrinking. Tear tests made on the same fabrics by other methods gave lower gains.

Curves for the tear tests of the 80 × 80 print cloths (Figure 9) show greater stretches at much higher loads for the shrunk fabric before tearing starts.

TABLE III. Comparisons of Breaking Strength and "Lengths at Break" (before and after Shrinking)

Sample		Warp		Filling	
		Breaking Strength (lb)	Length at Break* (%)	Breaking Strength (lb)	Length at Break (%)
7 Twill	Before	63.1	110.7	24.0	109.1
8	After	67.0	113.6	26.5	101.8
9 Plain	Before	41.2	113.3	30.5	108.8
10 weave	After	41.5	117.0	37.4	105.1
11 Print	Before	41.3	112.4	29.7	116.9
12 cloth	After	39.6	110.9	28.8	114.4
13 Osnaburg	Before	43.8	112.9	35.5	122.9
14	After	41.6	109.7	39.9	117.0
15 Bagging	Before	70.5	120.3	78.0	124.9
16	After	92.2	113.6	91.9	118.9

* Example: No. 13 broke at 112.9% of its original length; No. 14 (from Table I) shrunk 28%. Its retained length, 72%, multiplied by the elongation, 52.3%, gave a length at break of 109.7%.

Comparing Shrunk with Unshrunk Fabrics

When a fabric is changed in properties by high shrinkage, one of two comparisons is usually required. The simplest of these is comparison with the original cloth to see what has happened (Figures 2 and 3, and Tables I and II), but it is usually more important to compare with some other fabric over which the treated fabric is supposed to represent an improvement. Then the main difficulty is that practically everything about the treated fabric has been greatly changed—not only texture, but thread count, area, weight per square yard, and possibly the yarn numbers.

If the original fabric was acceptable for a given purpose, the same fabric shrunk is likely to be much too heavy. In order to evaluate it adequately with

TABLE IV. Tear Strengths before and after Shrinking

Material	Shrinkage		Tear Strength	
	Warp (%)	Filling (%)	Warp (lb)	Filling (lb)
Light Osnaburg, grey	—	—	10.3	7.9
Same, mercerized	28	30	20.1	13.6
80×80 print cloth, scoured	—	—	4.9	2.6
Same, mercerized	19	18	9.4	5.6

respect to a normal fabric, or to its probable behavior in service, it is necessary to follow one of two procedures. The first is to match a normal fabric as nearly as possible to the stretchable fabric obtained, and then make the comparison. The second is to compare the fabric that is already in service with a new one which, after shrinking, will match it in construction. Strict comparisons will still be impossible.

To make a comparison of the first kind, a fabric should be designed and woven with specifications as nearly as possible to those of the shrunk fabric. This means using yarns of the resultant numbers for warp and filling, and using the resultant numbers of ends and picks, as nearly as they can be estimated from the shrunk fabric, to obtain a result reasonably comparable with it. On the other hand, to match a given unshrunk fabric with one which should have over-all similar construction after shrinking, it is necessary to use finer yarns and to weave fewer ends and picks, in order to get a fabric which will shrink to approximately what is desired. It may be possible to devise and use a slack-mercerized fabric without very much trouble, but comparisons with other fabrics have little significance unless made on some such basis as suggested.

Effects of Caustic Soda Variables

From observations during general studies on mercerization, there has seemed to be little need for detailed special studies of the effects of the usual variables of caustic soda solutions with respect to slack mercerizing. Results so far from shrinking large or small pieces of fabrics of various constructions have been satisfactory at ordinary temperature, and at the usual caustic concentration of 22–23%. The time has usually been somewhat longer than in conventional mercerizing, but this may be unnecessary, and can be checked with reference to the particular types of fabric to be run.

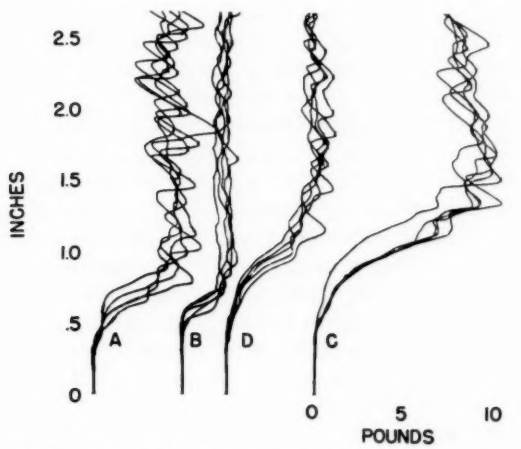

Fig. 9. Tearing behavior with print cloth. Before shrinking: *A*, warp; *B*, filling. After shrinking: *C*, warp; *D*, filling. (Trapezoid test; see Table IV.)

TABLE V. Shrinkage of Sheeting (72 × 62)

Treatment	Direction in Fabric: Warp (%)	Direction in Fabric: Filling (%)
Water only	2	0
Caustic soda, 15%	17.1	7.1
Caustic soda, 22½%	20	10

Bandage fabrics were, at first, treated with 30% caustic soda with the thought that more forceful swelling, due to the stronger caustic [7] would allow handling with less tendency to premature stretch. The use of 23% caustic in later work has been satisfactory.

One comparison has also been made with a caustic of lower strength, which showed that the higher swelling of fibers attributed to such caustic did not carry over into fabric. A desized, 72 × 62, 1.85 (yd/lb) sheeting gave the results shown in Table V. The shrinkage was greater with the stronger caustic, and, if a straight-line relationship is assumed, the difference was 0.4% for 1% change in concentration. Obviously, small variations in caustic strength have little significance.

Uses for Slack-Mercerized Fabrics

Various possible uses for slack-mercerized yarn or fabric have been described or suggested; and a few others will be suggested which would take particular advantage of their high stretchability and other elastic properties.

Fabrics with high stretch in only one direction should not be overlooked, but are not dealt with in this paper.

The two-way type of fabric may be useful for mere stretchability; for deformability or conformability, as one may look at it; or for stretching where a considerable degree of recovery is desired. An alternative is knitted fabric, but ordinary knitted cotton goods seem more readily distorted, and sometimes depend upon distortion of the piece as a whole,

as well as of the loops, for stretchability. For example, knitted bandages, when they were checked a few years ago, were found not as satisfactory as the gauze bandages made from woven cloth. There are too many constructions and degrees of stretchability possible, for a simple broad comparison between woven and knitted goods. However, it seems that the two-way stretchable woven fabric tends to hold either dimension better when stretched in the direction of the other dimension. Almost needless to say, very careful comparison should be made from a practical point of view if fabrics of two such different types are under consideration for a given use.

Construction, including that of its yarns, largely determines the utility of any slack mercerized woven fabric, but has apparently never been studied extensively in this connection. Again pertinent, however, are observations on bandage fabrics. Gauze made from yarns of the higher twists, within the limits found in commercial fabrics, was slightly more shrinkable, and shrunk fabrics made from it were more stretchable, than when the yarns had lower twists. To extrapolate a little, twist above average, at least in the warp, might aid in the retention of the shrinkage while the mercerized goods were being handled in the caustic soda and during washing; and high twist might also help in retaining stretchiness and elastic properties if the shrunk goods were to be wet or laundered during service.

The use of plied yarns in fabrics for shrinking does not, as judged mainly from yarn experiments, seem to offer any particular advantage over singles with respect to stretchability and elastic properties, but may help meet some special requirement.

Fabrics made more stretchable and more elastic by slack mercerizing might find uses in the making of garments, perhaps in place of cloth cut on the bias to obtain the effects of give or stretch; or might be utilized in bands, pads, etc., with less waste. If there are possibilities here, one of the most important questions will be whether the fabrics tend to stretch or bag after some length of time in service. They can be expected to withstand dry cleaning, but possibly not repeated laundering. It would seem, however, that fabrics constructed from yarns of suitable twist would reshrink to a degree upon wetting and drying, especially if they were parts of a garment. This is an untried field as far as known to the authors, and only practical tests will tell whether it has promise.

Shrunk-mercerized fabrics have been tried for use in molding plastics of irregular shape, but have probably not been studied for such uses sufficiently, and again, as far as known, have not been adopted in a practical way.

Base Fabrics for Coating

Several different leads have called attention to the possibility of using stretchy, slack-mercerized cloths as base fabrics for coating. The recent paper by Young [13], with particular reference to vinyl coating, with the accompanying extensive discussion, indicates that there is a complex group of problems in this field. It suggests, to one familiar with them, the trial of slack-mercerized fabrics although they were not mentioned in the paper. While the article gives some idea of desired properties, the actual requirements are apparently not any too well understood. There seem to be satisfactory fabrics for some purposes, and not for others; and the satisfactory fabrics are not all necessarily cotton, although Young considers cotton the best all-around fiber for fabrics to be coated.

The properties of the stretchy mercerized fabrics suggest three principal ways in which they might function when coated. (1) A highly stretchable fabric could stretch with the film of coating and relax or return with it upon release from stress without exerting any appreciable pull to help bring the coating back. This behavior alone would not seem to contribute much to the utility of a coated fabric. (2) A fabric after coating might return from stretch with sufficient elastic force to help bring the coating back with it. This possibility seems uncertain and might depend upon numerous conditions, but might be effective in some ranges of strain. (3) An approach to the ideal would seem to be a fabric which, in place under or within a coating, would have a load-elongation curve the same as that of the coating. That is, it would seem most desirable that the cloth and the plastic, as combined, have equal elongations so that as the composite structure approached the breaking point it would have the maximum possible breaking and tear strengths, with full utilization of the possible contributions of both materials. Experiments already mentioned suggest a good possibility of increased tear strength, but this would have to be confirmed after coating.

Stretchability is easily reduced or lost during the finishing of slack-mercerized fabrics. It was observed in the experimental drying of bandage fabrics on frames that almost no stretching could be allowed, to control the area of the fabric, without great loss of its essential properties. The straightening of

edges, control of width, and some control of stretchability may be effected by tentering, but this can easily result in a relatively great loss of stretchability.

The applicability of the coating to this new type of base fabric, without too much loss of its elongation, is assumed to be possible because knitted goods can be thus processed with retention of stretchability. The nature of the fabrics is such that less rather than any greater difficulty, would be expected in the anchorage of the coating to the fabric, as compared with ordinary cotton.

It thus seems quite possible that suitable fabrics mercerized with a high degree of shrinkage may help meet the needs brought about by new conditions of manufacture and of use of coated fabrics—particularly the need expressed by Young [13] for a woven fabric with two-way stretch, with better properties than knitted fabrics.

The suggestion has been made that cotton rugs and carpeting be mercerized in the piece to change their characteristics and improve them. In a few trials it was observed, as expected, that loss in area and gain in weight per square yard took place, to a degree determined largely by the original weight and closeness of weave (as well as by the rubber backing). The pile was shortened and tended toward better cover. There would be the usual difficulty in removing the caustic soda from such heavy goods. If followed immediately by piece dyeing before drying the goods would have unusually high affinity for dyes and, if they could be dyed level, would respond with a saving in dyestuff, or deeper shades more readily obtained. The carpet fabrics would, supposedly, have to be designed for shrinking. An eventual deciding factor in the use of such a process might be whether there would be more gain than could be effected by simply using more cotton.

The suggestion is sometimes made to weave a fabric from yarns mercerized slack beforehand, rather than to mercerize the cloth, and thus avoid some of the recognized difficulties. In the first place, it would undoubtedly be more expensive; and in the second, one would not obtain the same properties, and the resulting fabric would almost certainly not be usable for the same purposes as that shrunk directly. On the other hand, the fabric made from shrunk yarn might have some special properties which would adapt it to something else and justify its cost.

A fabric or webbing to take up shock, such as parachute webbing, is a possibility where it would not be clear without a trial whether to mercerize in the yarn or in the piece. The earlier work on tire cord suggested that, where weight is not too serious a consideration, a fabric might be designed to elongate considerably and with increasing resistance under a sudden load, short of the breaking load, to ease a jolt or shock. Making a webbing from suitable shrunk yarn might be preferable, with the easy stretch coming out at an early stage in handling. There are almost too many variables for a general study, but trial would seem worth while for a specific problem.

Acknowledgment

Most of the special tests on bandage fabrics were made by former members of the Modification Unit of the Cotton Chemical Processing Section. Recent tests on slack-mercerized fabrics were made by Miss Janice M. Poynot and Mrs. Ardis M. Keller of the Textile Testing Unit of the Analytical, Physical-Chemical and Physics Section. Special thanks are due John D. Tallant for data and curves from the Instron testing machine, and to George I. Pittman of the Engineering and Development Section for all the drawings.

Trade names are mentioned for convenience and information only and are not to be construed to be a recommendation by the U. S. Department of Agriculture.

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Pilot Plant Production and Properties of Cyanoethylated Cotton[1]

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TEXTILE fiber engineering has been aided in recent years by the improvement of natural fibers and the development of new textile fibers. Although much credit is due to the plant and animal breeders who have developed new varieties and strains, the present discussion is concerned primarily with the development of new textile fibers. The new textile fibers may be placed in three categories:

1. Man-modified natural textile fibers, characterized by the preservation of the intrinsic elements of fiber structure while conferring additional functional properties to the fiber.

2. Man-made textile fibers derived from natural textile fibers by chemical reactions which either permanently or temporarily modify the bonding forces between the intrinsic elements of fiber structure so that disruption may be induced, following which a new arrangement of certain of these structural elements into fibers may be effected.

3. Man-made textile fibers derived from synthetic polymeric materials which have certain structural features and functional properties characteristic of man-modified and man-made fiber derived from natural polymeric materials.

The discovery of the mercerization process by Mercer [29] in 1844, and the improvements by Lowe [26] in 1889 are illustrative of the early work directed toward the development of new textile fibers falling in the first category. A somewhat different approach to this problem involving the permanent attachment of various chemical groups to the basic unit of fiber structure of the cellulose molecule has been made in recent years. The two chemical processes which are now being explored on a pilot plant scale are cyanoethylation [12] and acetylation [18] of the cotton fiber. Since the cyanoethylation of cotton by treatment with acrylonitrile causes the least disruption of the intrinsic fiber structure, this method best illustrates this approach to the general problem of the chemical modification of cotton [10].

The first man-made fiber from nitrocellulose by Count Hilaire de Chardonnet [15] in 1884, as well as the fibers produced by the cuprammonium [39], viscose [14], and acetate [31, 38] processes are representative of the textile fibers in the second category.

The third category of fibers includes such textile fibers as nylon, introduced to the trade in 1938, and the more recently developed fibers Orlon (Du Pont

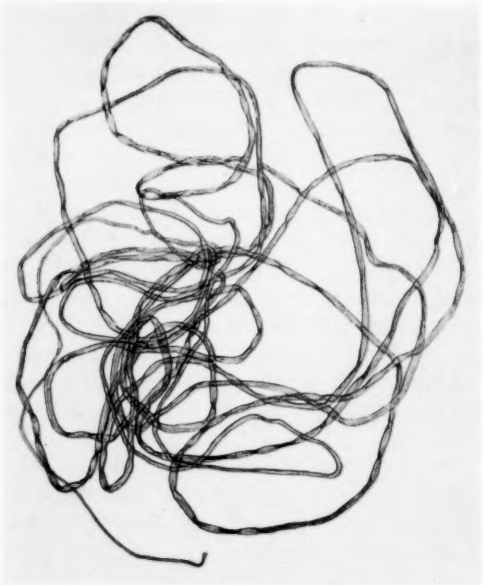


Fig. 1. Single cotton fiber, 1 1/16-in. staple.

Fig. 2. Single cotton fiber showing convolutions.

[1] The coined name "Azoton" has been given to cyanoethylated cotton by the Institute of Textile Technology.

acrylic fiber), Vinyon, Dynel, Acrilan, and Dacron (Du Pont polyester fiber).

Structural Properties of the Cotton Fiber

One of the outstanding structural properties of all textile fibers is that the length is very great with relation to the width, or thickness. In the cotton fiber this ratio is in the order of 1:2000 to 4000, depending on the fiber diameter and length. In Figure 1 this relationship is clearly shown. From an engineering point of view, it would appear at first glance that it would be impossible to make anything valuable from structural beams of these dimensions, yet the cotton mill man is able to construct useful and intricate fabrics from such elements with the aid of machines whose invention dates, in many cases, back to the Industrial Revolution of the eighteenth century. It will also be observed that there is a slight taper in the fiber from the base to the tip, but for the greater length of the fiber there is no perceptible change in diameter.

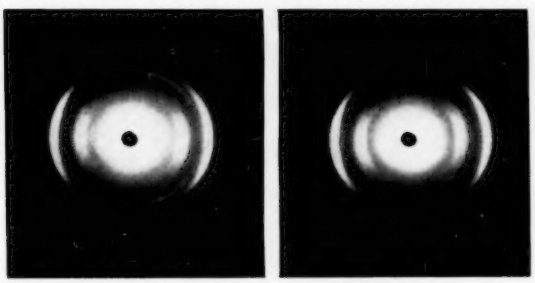
Another characteristic of cotton fibers is the convolutions, or twist, along the length. The net twist in the fiber is zero or very nearly so, since there is as much S twist as Z twist. As the moisture of the developing cotton fiber decreases, convolutions begin to appear, reaching a maximum shortly after the cotton boll opens some 55 days following flowering (Figure 2). It has been found in spinning that cottons containing the greater number of convolutions process easier. It is desirable therefore to preserve this property of cotton fibers.

Probing somewhat deeper into the structure of the cotton fiber, it has been shown by double refraction in polarized light and by X-ray diffraction patterns that cotton is composed largely of crystalline units. Thus, when a cotton fiber is examined between crossed Nicols, bands of extinction occur where the orientation of the crystallites reverses (Figure 3). This phenomenon may be strikingly shown in color by use of a selenite plate in the microscope. Varying color effects may be obtained, but second-order yellow and second-order blue are most prominent. These color effects may be reversed by rotating the fiber through 90°, the colors yellow and blue alternating along the length of the fiber [4].

A typical X-ray diffraction pattern of native cotton is shown in Figure 4*A*. The length of the two outer diffraction arcs (002 and 101 planes) indicates the deviation of the crystallite unit orientation from the fiber axis, when the inner diffraction arc (101 plane) is oriented parallel to this axis [41]. Thus, in general, the extent of crystallinity as determined by the sharpness of the diffraction pattern or lack of diffuse background, and the orientation of the crystallites with respect to the fiber axis, can be estimated.

Consideration should now be given to the arrangement of the crystallites in the cotton fiber in

Fig. 3. Swollen single cotton fiber in polarized light. *A*, Fibrils throughout most of length of fiber are arranged in spirals. Cross sections through such areas swell unevenly. *B*, At intervals the fibrils run parallel to the fiber axis, producing the familiar "area of extinction." Cross sections through these areas swell more evenly. (*Courtesy of Wanda K. Farr.*)



A *B*

Fig. 4. X-ray diffraction pattern of (*A*) native cotton fiber, (*B*) cyanoethylated cotton fiber, 1.8% nitrogen.

relation to other structural components. The structural elements of the cotton fiber are (1) primary wall; (2) secondary wall; and (3) lumen (Figure 5). The outside of the fiber is covered with a thin layer of wax, pectic material, and encrusting materials which are presumably calcium and magnesium salts of pectic acid.

Primary Wall

Some workers differentiate between the cuticle and the primary wall, whereas others consider these to be the same. The primary wall of the cotton fiber results from the extension of certain epidermal cells of the developing cotton seed. It reaches its maximum length about 20 days after the cotton flowers. From studies made on the outer limiting membrane of the fiber, removed by severe agitation using a Waring Blendor, the primary wall seems to be less than 0.2 μ thick and to be made up of laminated microfibrils [32, 43], 200 Å in diameter, although some fibrils are twice this diameter and some are as small as 100 Å. The first layer is oriented in a direction parallel to the fiber axis, whereas the second layer is oriented transversely [37]. Underneath this is a primary winding, or wide bands of microfibrils about 0.1 μ thick, which spiral around the fiber [21, 24]. Other workers have concluded that the cellulose in the primary wall is either randomly arranged [40] or that the fibrils lie transverse to the fiber axis [6]. The composition of the separated primary wall and that of the entire mature fiber [43] is shown in Table I.

The contribution of the primary wall to the weight of the cotton fiber has been estimated to be about 5%.

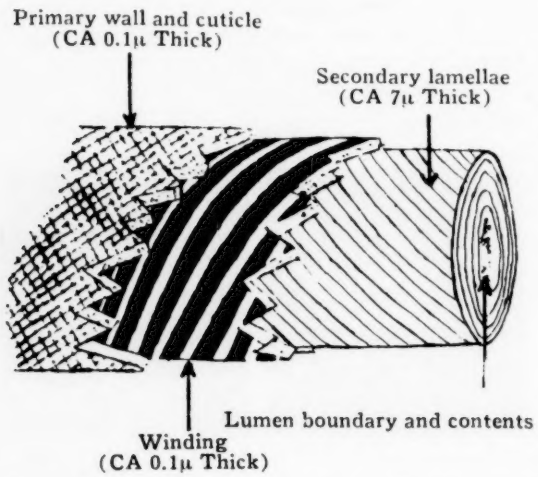


Fig. 5. Schematic representation of structural parts of cotton fiber. (*After Rollins.*)

Secondary Wall

The secondary wall constitutes the greater part of the cotton fiber and is composed of lamellae consisting of dense, and porous or less dense, areas (Figures 5 and 6). It is claimed by some workers that a lamella is deposited each day after the primary wall has reached its maximum elongation [5]; the dense area is deposited at night as the result of active photosynthesis of cellulose during the day, and the less dense area during the day—there being little photosyntheses during the night [23]. There would normally be about 30 to 40 lamellae in a cotton fiber regardless of fiber diameter. The so-called daily growth rings, or lamellae, are claimed to be analogous to the annual growth rings observed in the cross sections of trees, but are deposited in the inverse order. Considerable doubt exists, however, regarding the accuracy of these observations, since it has been pointed out that the "growth rings" may only be artifacts resulting from pressure on the cover glass of the microscopic mount of the highly swollen fiber cross section [16].

The existence of lamellae in the secondary wall remains unquestioned, but confusion exists regarding the number present. The observation that the number of lamellae in a fiber cross section is dependent upon the cell-wall thickness of the fiber appears to be logical. Thus, thin-walled fibers and very fine mature fibers would have fewer lamellae than either thick-walled or coarse mature fibers.

TABLE I. Chemical Composition of Typical Cotton Fiber and Primary Wall

Constituent	% of Dry Weight*	
	Fiber	Primary Wall
Cellulose	94	54
Protein (% N × 6.25)	1.3	14
Pectic substance	1.2	9
Wax (alcohol soluble)	0.6	8
Ash	1.2	3
Cutin/suberin (?)	—	4

* Moisture regain of fiber 8%; of primary wall 13%.

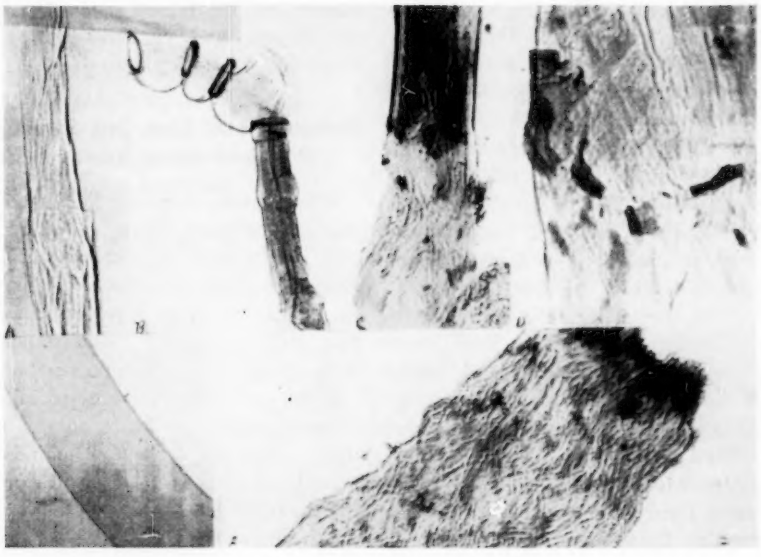


Fig. 6. Components of cotton fiber. *A*, Fifteen-day-old cotton fiber from which transparent outer membrane is partially removed. *B*, Effect of this relatively insoluble outer membrane during swelling of a dyed fiber in cuprammonium hydroxide. *C*, Partially removed outer membrane of a dyed cotton fiber affects swelling in cuprammonium hydroxide. *D*, Flakes of outer membrane upon the surface of a dyed cotton fiber during swelling in cuprammonium hydroxide. *E*, Hollow cylinder of outer membrane material from a mature cotton fiber shows its microscopically structureless nature at this magnification. *F*, Fibrillar structure of the secondary lamellae of a dyed cotton fiber from which the outer membrane had been removed during swelling in cuprammonium hydroxide. (*Courtesy of Wanda K. Farr.*)

Since each dense area of the lamellae has been observed to be about 1 μ thick and little changed by swelling agents in contrast to the less dense or porous areas, then the number of lamellae in a fiber 20 μ in diameter will be 8 or 9, whereas a fiber 10 μ in diameter will have 4 or 5. A cotton fiber is usually far from being perfectly cylindrical, but often has constrictions and distentions along its length. It would thus appear that the observation that the number of lamellae varies with the fiber diameter is more plausible than that the thickness of the lamellae varies with the fiber diameter—a necessary conclusion from the daily-growth-ring hypothesis. A correct understanding of the properties of the lamellae is very helpful in attempting to improve the physical properties of the entire fiber by selective chemical reactions. The two gross components of the lamellae should thus be given further consideration.

Amorphous or less dense area. Between successive crystalline areas lies an amorphous or less dense area. When the cotton fiber is treated with swelling agents, the amorphous area cementing the dense areas together increases in thickness to a much greater extent than the dense areas (Figures 5 and 6). This less dense area appears to be made up of amorphous cellulose or cellulose molecules in a disordered state. The molecules composing this area may not be of the structure ascribed to cellulose but rather hybrid molecules of cellulose with certain other foreign structural units of a nature similar to those comprising pentosans and uronic acids in the cotton fiber [11]. The possibility exists that this area is composed of disorganized ends of molecules or fringe from the organized crystalline component comprising the dense area. There is some evidence that indicates that the "cellulose" molecules in this area may be shorter in length and branched off the molecules comprising the dense crystalline area of the lamellae. The composition and chemistry of this component of the lamellae remain obscure, and further work is needed.

Crystalline or Dense Area. The portion of the lamellae which increases very little in thickness in the presence of swelling agents for the cotton fiber, upon examination in polarized light or by X-rays, is found to be crystalline in nature (Figures 3 and 4). This cylindrical sheath is composed of many long, continuous strands, or fibrils, aligned side by side and spirally wound around the fiber. When the ends of these fibrils are torn from the sheath, they have been found to be about 1 μ in diameter and possibly extending the length of the fiber (Figures 5 and 6). Occasionally, reversals of the fibril spirals occur in a given lamella, and some workers consider these to be potential weak spots along the fiber, whereas others do not. Some workers have found the fibrils to be as small as 0.3 to 0.5 μ in diameter [20], whereas others believe that they have no limiting or fixed dimensions but grade downward from about 1 μ to molecular dimensions [3]. The material separating and binding the fibrils together in a continuous sheath or shell is presumed to be similar to the material comprising the amorphous or less dense area of the lamella, regardless of fibril dimensions. The only exception to this is found when the fibril dimensions are reduced to those of the cellulose molecule, and in this case the binding force is ascribed to hydrogen bonding, van der Waals forces, or other forces operating at the molecular level. From X-ray and polarized light studies, as previously mentioned, it has been found that the fibrils in the secondary-wall lamellae alternate in the direction of spirality (Figure 4). This relation may not be precise, but it is sufficiently true so that the acute angle may be determined without difficulty. In general, cotton fibers showing the smallest angle between spiral layers with respect to the fiber axis are the stronger fibers [13, 42]. The acute spiral angle varies from 22° to about 45°.

Lumen

The cotton fiber when developing is a single cell organism with a nucleus and cytoplasm. As successive layers of the secondary wall are built up, the volume of the cytoplasm decreases. When the cotton fiber reaches maturity, about 35 days after the primary wall and cuticle cease to extend, syneresis begins. The cell sap is lost, and the residual protoplasm is left in the elongated opening in the center of the fiber [8]. This central opening in the fiber is known as the lumen (Figure 5). Upon purification the lumen dimension varies with both the variety and environmental conditions under which the cotton is grown [44].

Molecular and Unit Cell Structure of Cellulose and Arrangement in Fibrils

When cotton fibers are purified, extraneous materials are removed, leaving predominantly the structural elements of the secondary wall. At the same time short-chain molecules may be removed; these are similar to those remaining in molecular structure, with perhaps the cellulose molecules remaining being changed in some important respects.

When cotton fibers are subjected to the degrading action of acids, oxidizing agents, and enzymes or other complexes derived from microorganisms, the amorphous areas seem to be first involved, followed eventually by the slower-reacting crystalline or fibril sheath comprising the lamellae (Figure 4). In order to understand these reactions more completely, it is necessary to give consideration to the molecular constitution of cellulose and arrangement of the molecules in the unit cell of the crystalline area.

The elements of structure remaining to be discussed are: (1) cellulose molecules; (2) unit cell structure of the crystalline cellulose; and (3) the arrangement of these structural elements in fibrils.

Molecular Constitution of Cellulose

The accepted molecular constitution of cellulose [9] is shown in Figure 7. It will be noted that it is a polymer of anhydro-D-glucose units bound together by 1,4 oxygen bridges. The total number of anhydro-D-glucose units in the average molecule of native cellulose (n) from various sources has been reported [19] to be: for unbleached cotton linters, 9200; untreated cotton fiber, 6200; nettle fiber, 10,800; ramie, 11,300; and sulfite wood pulp, 2900. Other values in the range of 3000 to 4000 have been also reported, various methods being used for the determination of the molecular weight.

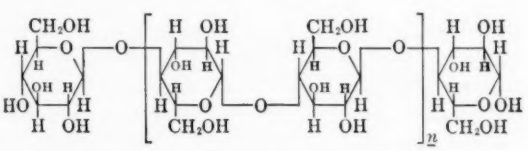


Fig. 7. Modern concept of cellulose molecule.

Another arrangement of the molecule [35] is shown in Figure 8. This concept of structure shows that the hydrated, open-chain form of cellobiose, in conjunction with the terminal open-chain D-glucose polymer units, holds the long anhydro-D-glucose polymer molecules together by hemiacetal linkages. Other simple sugars or sugar derivations may replace cellobiose in this scheme.

It will be noted that: (1) there are one primary and two secondary hydroxyl groups in each basic anhydro-D-glucose unit, the hydroxyls being in positions 2, 3, and 6; (2) the end glucose residues of each cellulose molecule are distinguished from those in the body of the chain by containing either an additional secondary hydroxyl group in position 4 or a reducing hemiacetal group in position 1; and (3) positions 1, 4, and 5 in each anhydro-D-glucose unit are involved in hemiacetal linkages.

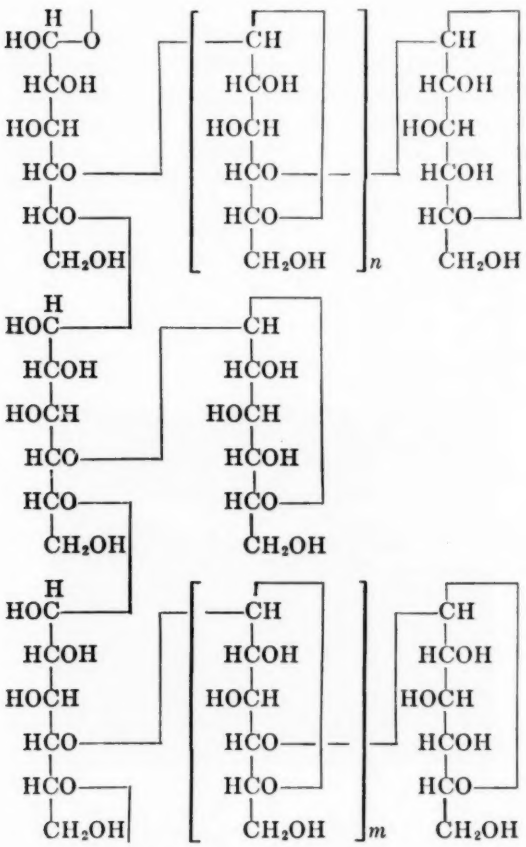


Fig. 8. Cellulose according to Pacsu concept.

Unit Cell Structure

The cellulose component of cotton fibers possesses the properties of an anisotropic crystal [33] which behaves toward X-rays as a three-dimensional grating and thus indicates a certain regularity of internal structure [36].

Long-chain or continuous theory. According to the long-chain theory the unit cell contains only a part of the cellulose molecule [22]. The dimensions of the unit cell of native cellulose as deduced from X-ray diffraction patterns [30] are indicated in Figure 9. It will be noted that every other cellulose molecule runs in the opposite direction. This is suggestive of the fact that permanent forces are operating which maintain this statistic balance. The crystalline units of cellulose are represented as repeat periods occurring along continuous chains of glucose residues which are arranged parallel to the *b* axis of the unit cell with a cellobiose group on each corner and one through the center. The cellulose molecules are held together laterally by secondary valence forces [28]. The anhydro-D-glucose units in the main valence chains are arranged alternately in such a way that a half turn occurs for each unit length. Adjacent chains in the *a-b* plane are arranged so that the primary hydroxyl groups, position 6, in one anhydro-D-glucose unit are next to the secondary

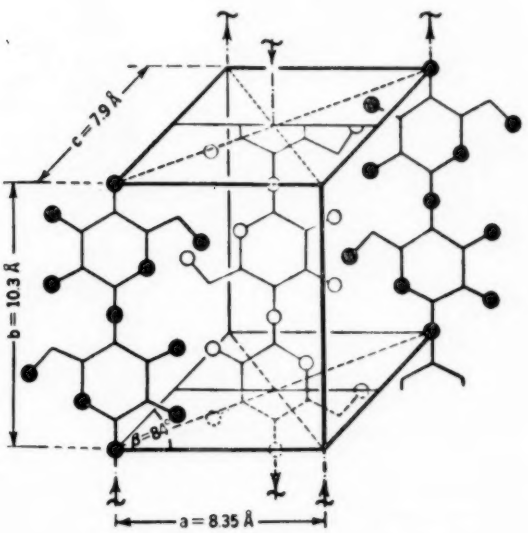


Fig. 9. Unit cell of native cellulose. (*Meyer and coworkers.*)

hydroxyl groups, position 3, in the anhydro-D-glucose unit of the neighboring chain. The centers of the two nearest oxygen atoms along the *a* axis of two anhydro-D-glucose units are about 2.5 Å apart. The close packing found is believed due to hydrogen bonding, since van der Waals forces would not cause an approach closer than about 3.0 Å, and compares roughly to a strength of 15,000 cal/mole.

Along the *c* axis the nearest distance between hydroxyl groups of adjacent chains is about 3.8 Å, corresponding to the distances that would be expected if van der Waals forces hold the molecules in this direction together. These forces correspond to a strength of about 8000 cal/mole.

Along the *b* axis, the main valence chains are held together by 1,4 glucosidic bonds. The strength of these bonds are of the order of 50,000 cal/mole.

It has been pointed out [41] that cellulose chains at different distances apart held together by three different kinds of forces in three different directions in space may be partly responsible for the important properties which cellulose fibers exhibit.

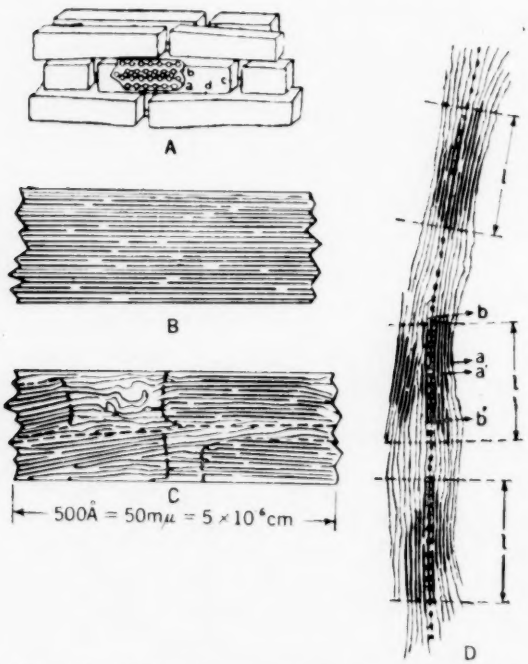


Fig. 10. Schematic representation of several possible crystalline structures (*Mark*). *A*, Micellar theory (*Seifriz*). *B*, Continuous-structure theory. *C*, Fringe-micellar theory. *D*, How main valence chains pass through more than one micelle (fringe-micellar theory). *a*, *a'*, *b'*, Molecule ends inside the crystallized region of one micelle. *b*, Molecule ends outside the crystallized region. *l*, Length of crystallized region.

Micelle or discontinuous theory. In contrast to the long-chain theory, the micelle theory accounts for imperfections in fiber crystallinity as being due to the presence of amorphous areas between discrete crystalline bundles of molecules. The long-chain or continuous theory is thus distinctly different from the discontinuous or micelle theory. In its original form [33] micelles were thought to consist of bundles of 40 to 50 chains of glucose residues each chain containing 100 to 200 anhydro-D-glucose units held together by either an amorphous cementing material or by tertiary forces similar in nature to van der Waals forces. The micelles of Nageli were thus below the limit of microscopic visibility. In contrast to this the cellulose particles of Farr and Eckerson [17] are microscopic, being 1.1 μ in diameter and 1.5 μ in length. According to the particle concept the fiber wall is made up mostly of particulate crystalline cellulose, which diffracts x-rays and is doubly refracting in polarized light, surrounded by a thin sheath of noncellulosic material which is non-doubly refractive and amorphous. The conclusion has been drawn by Farr that these are fundamental building units since the particles are observed in the living cytoplasm of young cotton fibers [16].

Arrangement of Cellulose Molecules and/or Unit Cell Structure in the Fibril

It seems that neither the continuous long-chain theory nor the discontinuous short-chain theory ade-

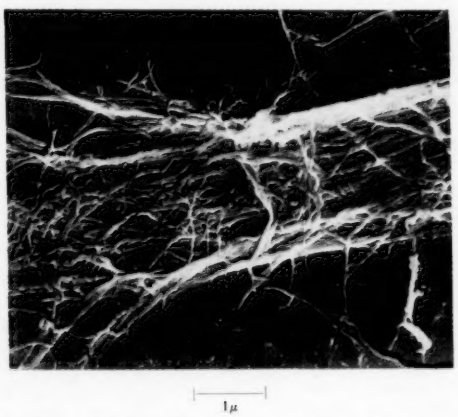


Fig. 11. Electron-microscope photograph of negative print of cotton linters beaten and chromium shadowed. × 12,000. (*Hercules Powder Co. photograph.*)

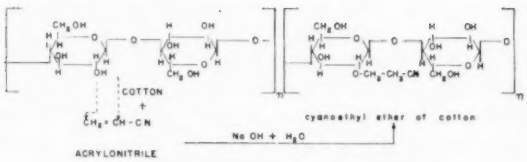


Fig. 12. Reaction of acrylonitrile with cotton.

quately satisfies all the accumulated evidence. It is now thought that discontinuities occur along the bundles of cellulose molecules either in some periodic manner or at random. These faults in the crystalline structure in either case result in fringe areas which may be thought of as amorphous cellulose. This is shown in Figure 10. Electron-microscope studies seem to indicate that the large fibrils, 1 μ and larger, found in the secondary wall of the fiber, may be broken and split into smaller fibrils. This process may continue until ultimately unit cell dimensions are reached. From X-ray studies, it is surmised that the ultimate micelle is about 50 Å wide and at least 500 Å long. Estimates from the chain length of hydrolysed cellulose [34] show that the more highly crystalline regions in cotton consist of 280 glucose units; i.e., they are about 1450 Å long. Within the limits of electron-microscope technique the diameter of the finest particle appears to vary in any one sample [25] (Figure 11). The approximate average diameters found were for cotton, 100 Å, and for cotton linters fiber, 160 Å. Evidence for the fine fibrils being aggregated into units of a larger size, such as fibrils several tenths of a micron in diameter, was not found. Although bundles near this size can be found, both larger and smaller bundles were also present. The fine fibrils seemed to be arranged in layers in the cotton fiber. These layers are reported to be about 0.1 μ in thickness.

Chemical Modification of Cotton Fibers by Cyanoethylation

From the above considerations the conclusion must be drawn that the cotton fiber has a very intricate structure that will probably never be duplicated in the laboratory. It would seem that the preservation of this structure would be most desirable, since the versatility of cotton is proof of the engineering value of nature's structure. In 1952 cotton alone accounted for 69.6% of the apparel-type fibers consumed in the United States [7]. Preservation of the performance characteristics [10] of cotton in any work directed toward chemical modification is thus essential. This of necessity means that the reaction conditions must be mild. In general, the amorphous areas of the cotton fiber are the most easily degraded part of the structure, yet these areas are also the first to react to form stable derivatives (Figure 4*B*). Chemical modifications which render these areas less susceptible to mechanical, chemical, and microorganism damage would thus appear to be desirable.

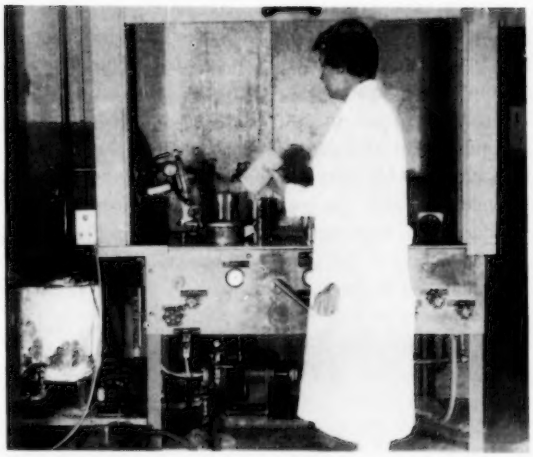


Fig. 13. One-pound Gaston County Package Machine in which preliminary studies were made.

Of the various chemical reactions investigated during the past five years at the Institute of Textile Technology [10, 12], the reaction of acrylonitrile with cotton causes the least change in morphological structure. This reaction may be represented as shown in Figure 12. The mechanism of the reaction of acrylonitrile with cellulose has been discussed in detail by MacGregor [27].

Treatment of Yarn in One-Pound Package Machine

The most convenient commercial processing equipment for treating cotton yarns and bulk fibers with acrylonitrile is the package dyeing machine. In preliminary investigations, a Gaston County single-package dye machine was used successfully (Figure 13). The procedure used with the one-pound package unit was as follows: A 1-lb package of 40s/2 combed yarn wound in the customary manner for dyeing was placed in a Gaston County dye machine. The machine was then charged with a 1.5% sodium hydroxide solution containing 0.1% Tergitol P-28.

The caustic solution was circulated through the package from inside out, and then the direction of the flow was reversed to outside in. The reversal of the flow through the package was effected by manual operation in 2-min cycles. After allowing the caustic to circulate in this manner through the package for 15 min at room temperature, it was drained off and the yarn package removed. The package was then centrifuged to reduce the dilute caustic pickup of the yarn to approximately 70% and then replaced in the machine.

The machine was charged with acrylonitrile and the expansion tank cut out of the circulating system by closing the expansion tank return and cutoff valves. The acrylonitrile was then circulated through the yarn package, using the same time cycles as for the caustic, while the reaction temperature was rapidly raised to the desired temperature by introducing steam into the steam jacket. The pressure developed in the kier as a result of thermal expansion of the acrylonitrile was relieved by opening the expansion tank return valves momentarily.

The reaction temperature was maintained at 135°F for 1 hr, after which the acrylonitrile was drained off and the yarn washed with cold water. A wash consisting of sufficient dilute acid to neutralize the remaining sodium hydroxide was then introduced, after which the package was washed free of acid in the machine. The yarn package was removed from the machine and allowed to dry in warm air. An analysis of the dry yarn showed that it contained 3.8% nitrogen.

Yarns Treated in 50-Package Machine

In runs made in the 50-package Gaston County dye machine, automatic controls were used (Figure 14), and the outside in-inside out circulation cycles were 5 and 3 min, respectively. The dilute caustic pickup in the case of both 60s/2 and 80s/2 cotton yarns wound on springs after centrifuging was 87%. The amount of acrylonitrile used in this machine was approximately 50 gal. The procedure used with the 50-package machine was otherwise the same as that employed in the case of the single-package dyeing machine.

A pilot plant making use of a modified 50-package Gaston County dye machine complete with an acrylonitrile recovery system has recently been put into operation by the Institute. This pilot plant was installed by the American Cyanamid Company at the National Plant of Standard-Coosa-Thatcher Company, Rossville, Georgia. This represents the first pilot plant to be designed specifically for the chemical modification of cotton and installed in a cotton processing mill (Figures 15 and 16).

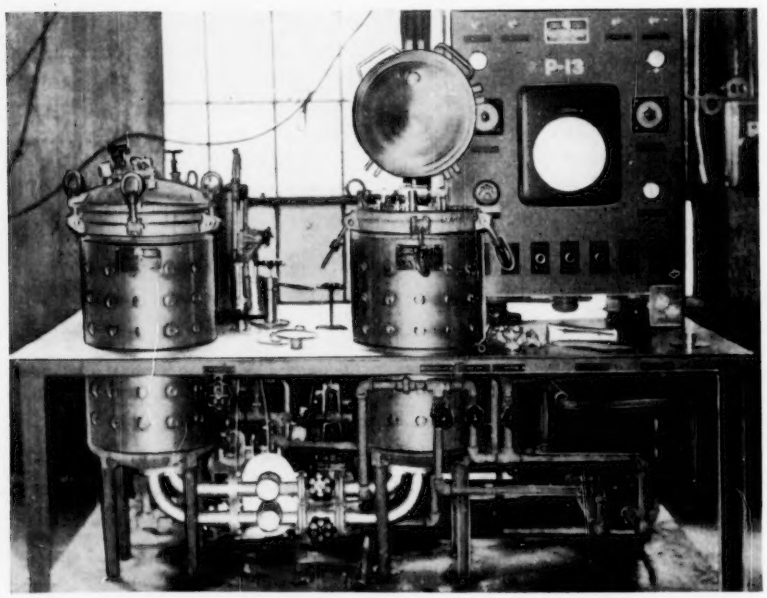


Fig. 14. Conventional 50-package Gaston County dye machine used for treatment of cotton yarn with acrylonitrile at the National plant of Standard-Coosa-Thatcher Co., Rossville, Ga.

Bulk Fibers and Fabric

It has been found that cotton fibers in bulk form may be successfully treated in a Gaston County dye machine using the bulk fiber adapter. Full-width fabric, after proper folding, can be wrapped around the spindle of the dye machine and cyanoethylated successfully using essentially the same procedures described. In all cases, uniform products were obtained by this method.

Another method which has been successfully used for the treatment of fabric on a continuous basis involves padding on of dilute caustic followed by immersion of the fabric in several tanks of acrylonitrile equipped with squeeze rolls. When the temperature of the acrylonitrile-water azeotrope is held at near the boiling point, 71–72°C, 2 to 3% nitrogen can be fixed to the cotton in a contact time of 2 to 3 min.

After the acrylonitrile treatment, the fabric was

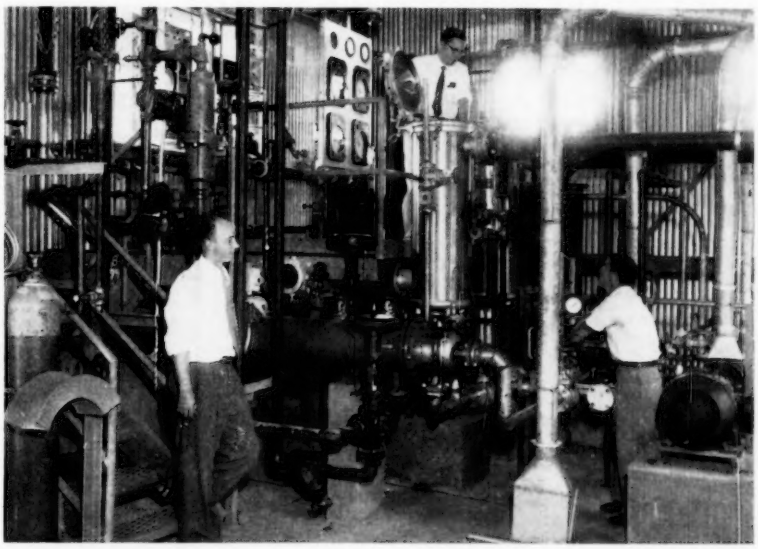


Fig. 15. Pilot plant for cyanoethylation of cotton, Standard-Coosa-Thatcher Co., Rossville, Ga. Inside view.

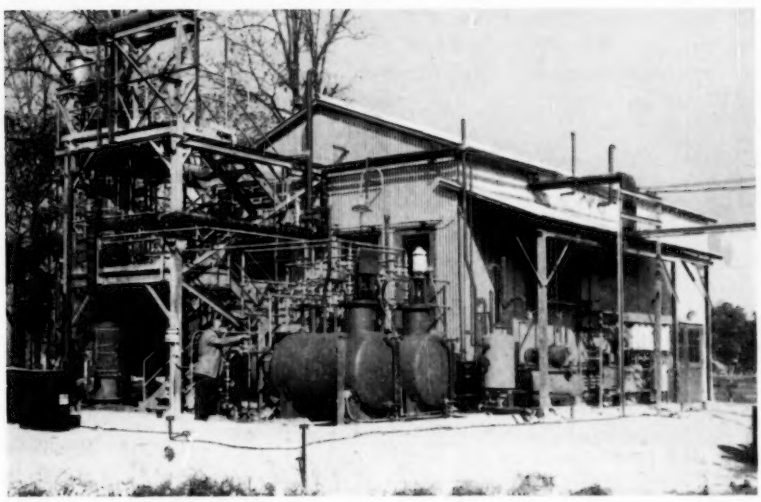


Fig. 16. Pilot plant for cyanoethylation of cotton, Standard-Coosa-Thatcher Co., Rossville, Ga. Outside view.

passed into a cold-water wash and then into an acetic acid sour followed by additional cold-water washes. This procedure can doubtlessly be adapted to commercial production when a completely enclosed unit has been developed.

The vapor-phase reaction of caustic-pretreated cotton fabric with acrylonitrile has also been shown to be feasible, but a completely satisfactory production unit has not been developed.

Rate of Reaction of Caustic-Pretreated Cotton Fibers with Acrylonitrile

The extent of reaction of cotton fibers in bulk, yarn, or fabric form is conditioned by the thoroughness of the pretreatment and the concentration of the sodium hydroxide solution, the temperature of the acrylonitrile, and the time of contact with acrylonitrile. The rate of the reaction of acrylonitrile with caustic (2.0%) presteeped cotton fibers in the form of roving at 55°C is shown in Figure 17.

It will be noted that the reaction is initially quite fast, after which it slows down rapidly. The control of the nitrogen content is relatively easy in the range of 3% to 4%, which, in general, makes the most desirable product.

Properties of Cyanoethylated Cotton

Moisture Regain

The introduction of the first cyanoethyl groups into the cotton causes a slight increase in moisture regain, after which a progressive decrease occurs. In the most useful range of 3 to 4% nitrogen, the moisture regain of the new fibers is 2.5% lower than that of untreated cotton. This relationship is shown in Figure 18.

Strength and Elongation

In general, the tensile strength of partially cyanoethylated fibers with a nitrogen content of 5%, or less, is the same as that of the original cotton, as determined from single-fiber strength measurements. This is also true of the elongation. However, when the Pressley fiber bundle strength was determined, a strength increase was found. When calculated on the basis of grams per denier, no change in strength was found. Thus the strength increase found in this case was proportional to the weight increase due to reaction. When the extent of reaction exceeded

TABLE II. The Single-End Strength and Elongation of Partially Cyanoethylated Combed Cotton Yarns

Yarn Count		% Nitrogen Content	Breaking Strength		Increase in Breaking Strength (%)	Elongation (%)
Designated	Actual		(g)	(g/den)		
40/2	39.3/2	0	558	2.06	—	4.5
40/2	34.5/2	3.8	736	2.39	+16	6.5
60/2	58.8/2	0	318	1.76	—	5.0
60/2	55/2	3.4	410	2.15	+22	5.5

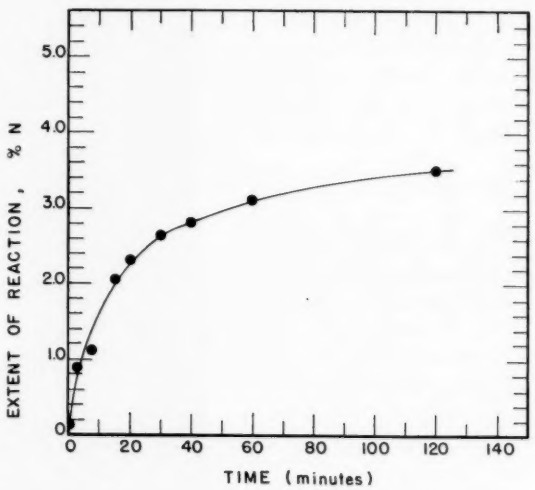


Fig. 17. Rate of reaction of acrylonitrile with cotton at 55°C (131°F).

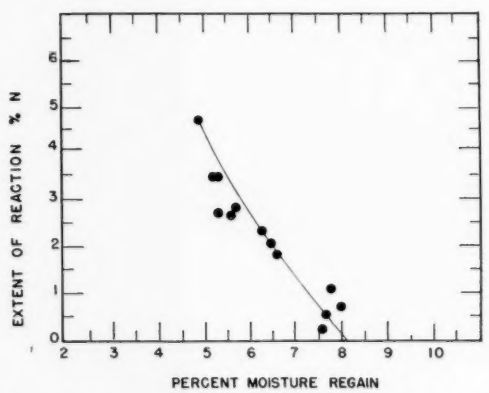


Fig. 18. Equilibrium moisture regain of cyanoethylated cotton fibers of various nitrogen contents conditioned at 72°F and 59% R.H.

a nitrogen content of about 5%, a progressive decrease in Pressley tensile strength occurred.

On the other hand, cyanoethylated cotton yarns, prepared in the package dye machine, were found to have greater strength and elongation than cotton yarns of the same count. The increase in strength was in this case decidedly greater than the weight increase. This effect on two different yarn counts is shown in Table II.

It will be noted that the strength increase of yarns is quite variable and has no direct relation to the extent of reaction. The conditions under which the reaction occurs seem to be related to the strength increases realized.

The breaking strength of cyanoethylated cotton fabric is usually about the same as that of cotton fabric of comparable weight and construction.

Appearance in Cross Section

Microscopic examination of fiber cross sections of the partially cyanoethylated and native cotton shows that the cell-wall thickness of the former is greater than that of the latter. In general, the lumen diameter increases at the same time that the fiber diameter increases. The increase in the diameter of the fiber is roughly proportional to the weight increase due to reaction with acrylonitrile. Photomicrographs of partially cyanoethylated 40s/2 cotton yarn containing 3.8% nitrogen and of the untreated original cotton yarn are shown in Figure 19.

Resistance to Microorganism Attack (Soil-Burial Test)

The most drastic condition for evaluating the resistance of textile materials to microorganism attack which has been developed is the soil-burial test. In this test, the fabric is subjected to the attack of both bacteria and fungi. The soil used in these tests at the Institute was composed of Virginia clay, sand, and peat moss mixed together to make a porous mixture described as a "good potting soil." This mixture was inoculated with spores of cellulose degrading fungus *Chaetomium globosum* and the surface growing fungus *Aspergillus niger*, after which it was stored in an incubator at 95% R.H. and 30°C. The moisture content of the soil was maintained at 25%, and the *p*H at 7 to 8.

Samples of partially cyanoethylated cotton duck and cotton duck 1¼ × 6 in. were placed in the soil vertically so that about 1 in. of the fabric protruded from the surface. After 7 days, the samples of cotton duck were removed; and, if they had lost at least 90% of their original strength, the soil was considered active, and the partially cyanoethylated duck

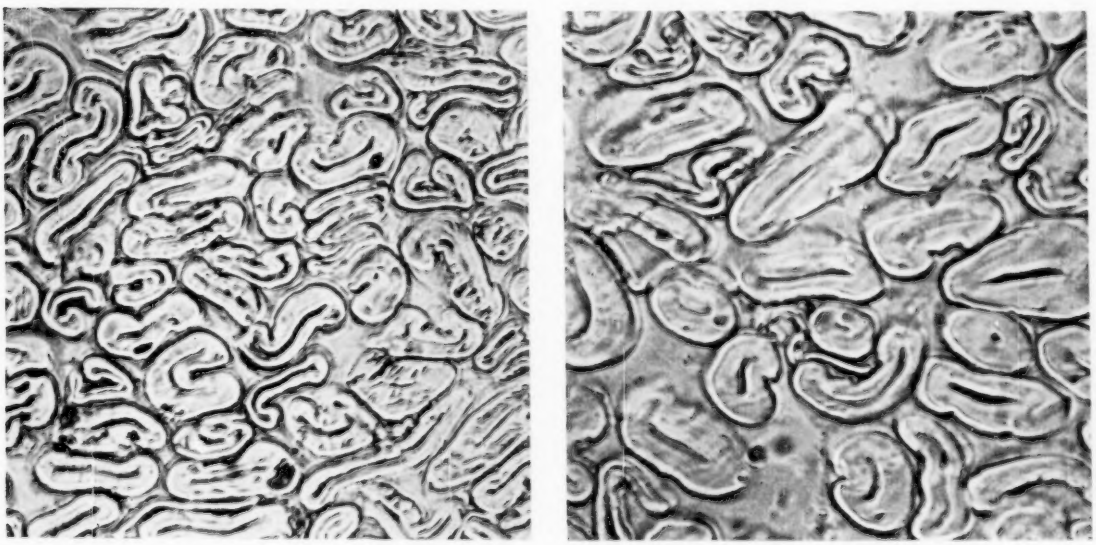


Fig. 19. Cross-sectional appearance of cyanoethylated cotton fibers (3.8% N) and cotton fibers taken from the same fiber blend. × 867.

strips were allowed to remain buried for an additional week.

At the end of 2 weeks, the cyanoethylated duck samples were removed, washed, dried, and the tensile strength determined on 1-in. raveled strips. The change in strength in comparison with the unburied cyanoethylated duck was then calculated. The appearance of the cyanoethylated duck samples after 2 weeks' soil burial along with that of cotton duck samples after 1 week's soil burial is shown in Figure 20.

The loss in strength of the cyanoethylated duck after 2 weeks' soil burial as a function of the extent of reaction with acrylonitrile is shown in Figure 21.

It will be noted that, when the nitrogen content of the cyanoethylated duck was within the range of 3.0 to 3.5%, no loss in strength occurred, whereas after 1 week the cotton duck had lost 100% of its strength in soil burial. Tests extending over periods of 6 to 12 months have shown similar results. In many cases significant increases in strength have been found after soil-burial tests on cyanoethylated cotton fabrics.

Deterioration tests on cotton yarns were run in a similar manner except that it was necessary to fasten the yarns in a frame during soil burial to prevent loss in twist; 40s/2 and 60s/2 cyanoethylated yarns containing 4.8% and 5.2% nitrogen have been found to suffer no loss in strength after 2 weeks' soil burial. Yarns containing as low as 3.5% nitrogen have been found to behave in a similar manner.

Resistance to Heat Degradation

The cyanoethylated yarn and fabric have been found to be resistant to both wet and dry heat degradation. In general, the cyanoethylated cotton products containing 3.0 to 5.0% nitrogen have been found most resistant to heat degradation.

The following procedure was employed in making tests for dry heat degradation: 8-oz cyanoethylated duck and cotton duck test strips 1¼ × 6 in., as well as 60-yd skeins of cyanoethylated and cotton yarns, were used to determine the effectiveness of the treatment. The test samples were leached in cold running water for 8 to 15 hr prior to testing, after which they were dried and placed in a forced-air circulating oven for the designated period of time at the desired temperature.

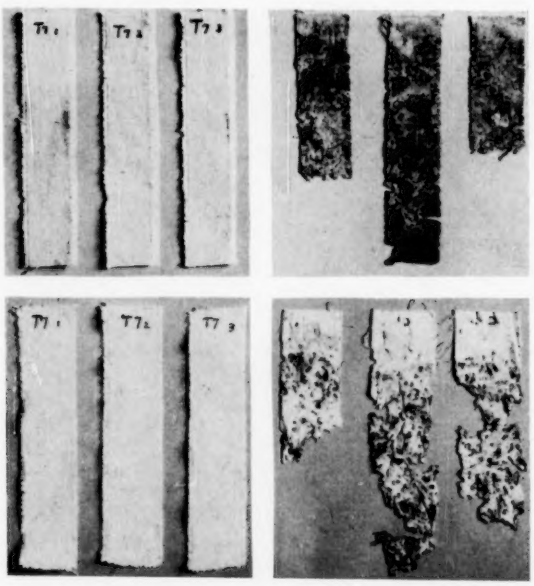


Fig. 20. A comparison of the appearance of cyanoethylated cotton (left) and cotton fabrics after burial in soil at 30°C and 95% R.H. for 2 weeks. *Top*, duck; *bottom*, print cloth.

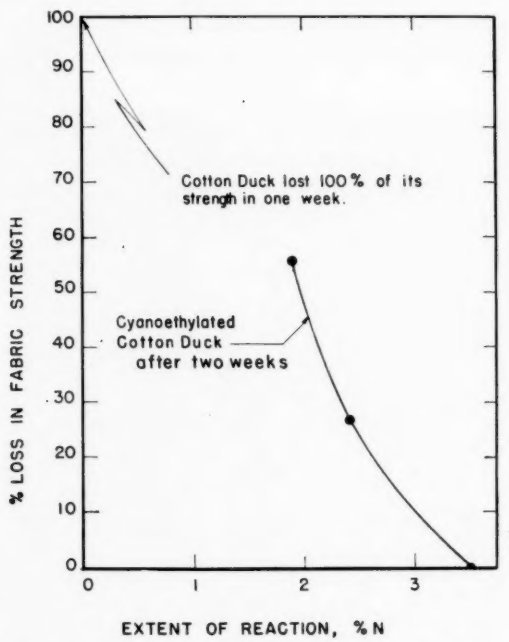


Fig. 21. Loss in tensile strength of cyanoethylated cotton fabrics of various nitrogen contents during 2-week soil-burial test.

The 1-inch raveled strip tensile strength of the fabrics and the single-end tensile strength of the yarns were then determined and compared with the original strength of the material. The nitrogen content of the cyanoethylated cotton duck in the test was 2.6%. The duck was heated at 160°C (320°F) for periods varying from 15 to 96 hr, as shown in Figure 22.

It will be noted that, although the cyanoethylated duck loses strength during this test, the loss is considerably less than that for cotton duck. The difference in loss in strength appears to be somewhat greater (45%) during the first 15 to 40 hr of heating than subsequent to this time (25%).

The effect of the extent of the reaction of cotton yarns with acrylonitrile on the resistance to heat degradation at 160°C after 15 hr is shown in Figure 23.

It will be noted that, whereas the untreated yarn lost about 65% of its strength under these conditions, yarns containing in the range of 2.5% to 5.0% nitrogen lost only 0 to 20% of their strength.

Resistance to Acid Degradation

Partially cyanoethylated cotton fiber, yarn, and fabric are degraded by both mineral and organic acids less extensively than the corresponding cotton item. This is shown in the case of sulfuric acid at concentrations by weight of 10, 20, and 40% with kiered and bleached cotton print cloth (80 × 80) cyanoethylated to nitrogen contents of 1.7, 3.5, and 5.9% (Figure 24). It will be noted that, as the nitrogen contents of the cyanoethylated cotton fabrics increases, the loss in strength after 20 hr immersion in the sulfuric acid solutions at 58–60°C decreases. Upon increasing the acid concentration the rate of degradation of untreated and cyanoethylated cotton fabric increases. Evidently the mechanism of hydrolysis of cotton is definitely modified by the presence of cyanoethyl groups in the more vulnerable amorphous component of the fiber.

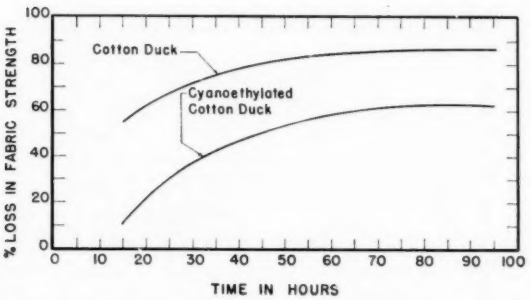


Fig. 22. Loss in strength of cyanoethylated cotton (2.6% N) and cotton duck during heating at 160°C (320°F) for various lengths of time. The same types of curves are obtained when yarns are tested.

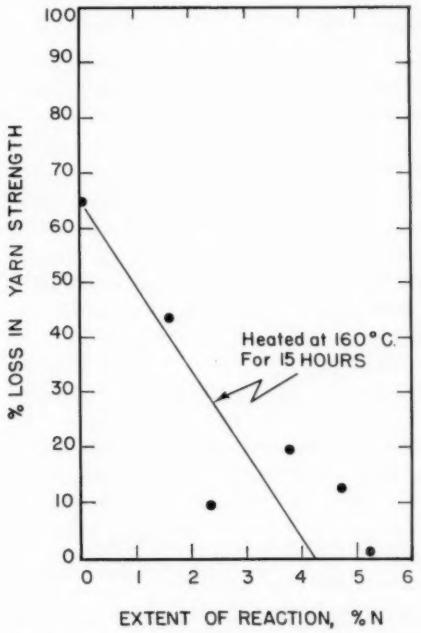


Fig. 23. Loss in strength of cyanoethylated cotton yarns of various nitrogen contents during heating at 160°C (320°F) for 15 hr.

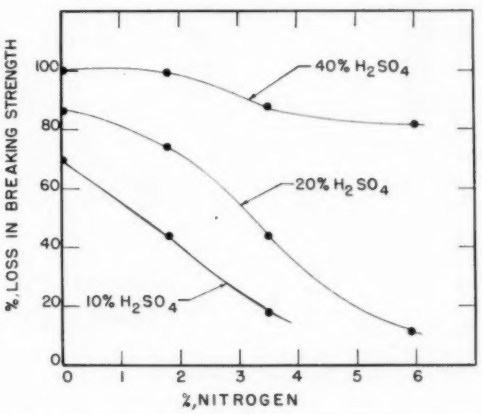


Fig. 24. Resistance to acid degradation of cyanoethylated cotton fabric treated for 20 hr at 58–60°C.

TABLE III. Per Cent Loss in Breaking Strength of Cyanoethylated Fabrics with Various Acids at 58° to 60°C for 20-Hr Exposure Periods

Fabric	Hydrochloric (10%)	Hydrochloric (20%)	Hydrochloric (38%)	Nitric (10%)	Nitric (20%)	Nitric (40%)	Sulfuric (10%)	Sulfuric (20%)	Sulfuric (40%)	Acetic (75%)
Control	95.0	100	100	84.0	100	—	70.0	86.0	100	13.0
1.7% N	85.0	100	100	70.0	88.0	100	44.0	74.0	100	5.0
3.5% N	60.5	100	100	49.0	76.0	100	18.0	44.2	88.0	4.0
5.9% N	45.0	100	100	46.0	66.0	100	11.0	11.0	82.0	1.0

Upon extending this work to include hydrochloric, nitric, and acetic acids the same conclusions may be drawn (Table III). In the case of acetic acid only one concentration, 75%, was investigated. The order of hydrolysis rates of untreated and cyanoethylated cotton by the mineral acids was found to be: hydrochloric>nitric>sulfuric acid. Acetic acid gave less strength loss at 75% concentration than any of the mineral acids at concentrations of 10%, with both a given cyanoethylated cotton fabric and the untreated cotton fabric.

Abrasion Resistance

Extensive tests made by the U. S. Quartermaster Corps have shown a good correlation to exist between service wear tests of fabrics and the Stoll flat abrasion tests. Stoll flat abrasion tests were, accordingly, used for evaluating the abrasion resistance of cyanoethylated cotton fabric. The abrading surface was 180-grit aluminum oxide cloth, the overhead weight was ½ lb, and 4 lb of air pressure was used to inflate the diaphragm under the fabric. The number of cycles required to abrade through the fabric was then determined, and the per cent increase in abrasion resistance calculated using cotton fabric of approximately the same weight as a control.

The effect on the abrasion resistance of the extent of reaction of 80 × 80 print cloth with acrylonitrile to produce partially cyanoethylated cotton fabrics was then calculated. The results obtained are shown in Figure 25.

It will be noted that, in general, the Stoll flat abrasion resistance of the fabrics increased as the nitrogen content of the cyanoethylated cotton fabrics increased. This finding is of considerable practical importance since increased wear of garments may result from clothing made from cyanoethylated cotton fabrics.

In many service uses flex abrasion resistance is of equal or greater importance than flat abrasion resistance. The flex abrasion resistance of cyanoethylated cotton with various nitrogen contents was thus determined using the Stoll abrader, and the data obtained were compared with untreated kiered and bleached cotton fabric (80 × 80 print cloth). The data obtained are summarized in Figure 26. It should be pointed out here that no finish of any kind had been put on the cyanoethylated cotton fabric, and that both the Stoll flat and flex abrasion data can be drastically changed by application of these materials in small amounts. In the case of the flex abrasion tests it will be noted that cyanoethylated cotton rapidly loses resistance to flex abrasion until

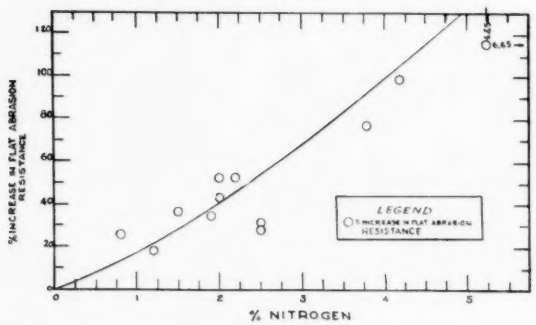


Fig. 25. The effect of fabric nitrogen content upon the Stoll flat abrasion resistance of cyanoethylated fabric.

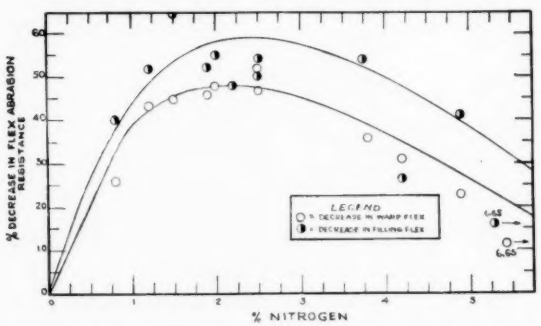


Fig. 26. The effect of fabric nitrogen content upon the Stoll flex abrasion resistance of cyanoethylated fabric.

a nitrogen content of 1.5 to 3.0% is attained, after which the loss decreases. Thus, when a nitrogen content of 5% is reached the loss in flex abrasion is only 23% compared to 45% at 2.5% nitrogen in the fabric warpwise direction. The significance of these data with relation to use in service has yet to be determined.

Launderability

Launderability of partially cyanoethylated kiered and bleached cotton fabric (80 × 80 print cloth) was determined by obtaining the strength loss in multicycle wash tests using the Launder-O-Meter, a machine that simulates the home laundry. One set of cyanoethylated fabric, 3.5% nitrogen, and untreated fabric samples were washed six times for 45 min each in a bath, at 160°F, containing 0.15% soap and 0.10% sodium carbonate. Another set of samples was washed under the same conditions, but with the addition of 100 ppm of chlorine. The untreated fabric lost about the same tensile strength after washing both with and without chlorine. The cyanoethylated cotton fabric washed in the soap bath containing chlorine lost about the same strength as the untreated fabric, while those washed without chlorine retained almost all their original strength (Figure 27). More extensive laundry tests have also shown no loss in nitrogen content of cyanoethylated cotton fabrics when laundered under normal conditions for cotton fabric and no loss in resistance to mildew attack.

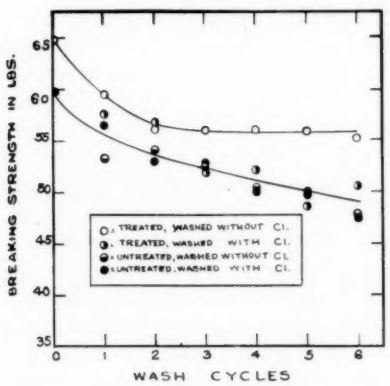


Fig. 27. Effect of multicycle laundering on the tensile strength of untreated and cyanoethylated cotton fabric.

Dye Properties

It has been found that cyanoethylated cotton fiber, yarn, and fabric are more receptive than similar cotton items to many dyes in all classes of dyestuffs. This increased receptivity is manifested both by a greater rate of dye pickup from the dye bath and a greater extent of exhaustion of the dye bath. Since the cyanoethylated cotton fabric with nitrogen content of 1.5% more completely exhausts the dye bath, a lower concentration of dyestuff in the bath is required to give the same shade as that obtained for cotton fabric, as shown in Figure 28.

A listing of representative dyes which have been tested on cotton and cyanoethylated cotton 80 × 80 print cloth to obtain the same shades is given in Table IV. The cyanoethylated cotton fabric used in this test contained 1.5% nitrogen. It will be noted that, in general, 33 to 60% less dyestuff was required to produce the same shade with the cyanoethylated cotton fabric as for the cotton fabric. In some cases, the lightfastness of the cyanoethylated cotton dyed fabric was slightly less than that of the cotton fabric; but with most dyes, it was found to be at least equal. Both washfastness and wet and

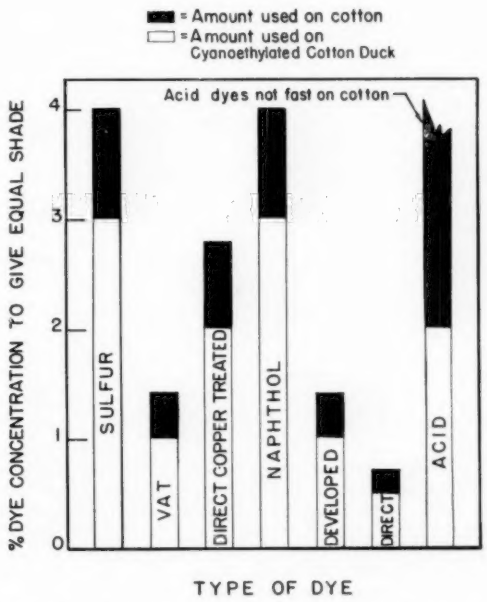


Fig. 28. A comparison of the amount of dye used on cyanoethylated and cotton fabrics to obtain equal shades. The dyes are the same as those described in Table IV.

dry crocking for the cyanoethylated cotton and cotton fabrics were found to be equal for all classes of dyes tested.

In general the affinity for most direct dyes decreases as the nitrogen content of the cyanoethylated fabric increases, whereas the affinity for acetate and acid dyes increases.

It should be stated that cyanoethylated cotton is an easily dyed fiber, but dyeing procedures must be developed in this case as has been true with every new fiber. Since the dyeing properties of cyanoethylated cotton vary with the extent of reaction, as shown by the nitrogen content, it is essential that uniformity of reaction be achieved if level dyeing is to result. Considerable work has been done by the Calco Division of American Cyanamid Company on cyanoethylated cotton yarns and fabrics supplied them by the Institute, directed toward developing satisfactory dye procedures (see page 84 of this issue).

TABLE IV. Comparison of Dyeing Properties of Cotton and Partially Cyanoethylated Cotton (80 × 80) Print Cloth *

Type of Dye	Name	% Decrease in Dye used for Cyanoethylated Cotton Fabric	Lightfastness†
Sulfur	Sulfogen Golden Brown RCF	33	—
Vat	Ponsol Blue GDD	40	+
Direct	Pontamine Fast Green 5BL	40	—
Direct (copper after-treat)	Coprantine Blue BLL	40	+
Naphthol	ASSW with Red Salt B	33	+
Developed	Rosanthrene Red 9BL developed with β-Naphthol	40	—
Basic	Victoria Blue B without mordant	60	+
Acid	Cloth Fast Brilliant Red 38W	—	+

* Various types of dyes were used in concentrations required to obtain same shades. The cyanoethylated cotton fabric used in this test contained 1.5% nitrogen. Ratio of dye liquor to fabric in all cases was 50:1. The concentration is based on the weight of dyestuff to weight of goods. Washfastness and wet and dry crocking were equal for both cotton and cyanoethylated cotton fabrics.

† + means cyanoethylated cotton was equal to or better than cotton fabric in Fade-O-Meter test. — means cyanoethylated cotton was not as good as cotton fabric in Fade-O-Meter.

Cyanoethylated Cotton Fibers as a Basic Raw Material

Treatment of cyanoethylated cotton fibers, yarns, and fabrics with various types of swelling agents for cellulose results in the enhancement of certain of the enumerated properties. The use of partially cyanoethylated cotton as a basic fiber material for further treatment thus opens new approaches to the problem of engineering textile fibers to achieve desirable end use products.

Handling of Acrylonitrile

Although acrylonitrile is toxic, flammable, and forms explosive mixtures with air [1, 2], the fact that millions of pounds are handled each year without accident is proof that it is not unduly dangerous if reasonable safeguards are taken. It is quite essential, however, that operating personnel be conversant with the hazards involved in handling this material so that they may take the necessary precautions. It is recommended that any mills wishing to use this process contact either the Institute or one of the producers of acrylonitrile.

Market Evaluation Program

Two chemical firms which are major producers of acrylonitrile are working with the Institute of Textile Technology and its member mills to determine the best means of producing and marketing cyanoethylated cotton textiles.

One concern, American Cyanamid Company, supplied and installed the equipment for a pilot plant which started operation early in October at Rossville, Georgia, in facilities provided by a member of the Institute, Standard-Coosa-Thatcher Company.

An estimated 20,000 lb of cyanoethylated cotton yarn and fiber will be produced at Rossville under the supervision of the Institute during a 9-month period, and will be processed by the member mills of the Institute into some 35 end uses, including industrial fabrics, clothing, home furnishings, and other textile items, for market evaluation.

Working similarly with the Institute, Monsanto Chemical Company, and another Institute member firm, Fulton Bag and Cotton Mills, Atlanta, Georgia, have completed preparations for operating a semiworks plant at Texas City, Texas, for producing some 10,000 to 20,000 yd of cyanoethylated cotton fabric for market evaluation.

Further extension of the value of the pilot plants is expected to come from the establishment of the optimum processing conditions for obtaining fibers, yarns, and fabrics best suited for specific end uses at the lowest cost. From the information obtained in the pilot plants and the market evaluation program, the future of the development can be determined.

The Institute intends to make the process available to the textile industry at the proper time through a licensing arrangement based on patents pending.

Acknowledgment

The work herein reported on the cyanoethylation of cotton has been carried out during the past 5 years with the assistance of a research team composed of Mildred Wetzel, Jerry Garrett, William R. Musick, Dr. D. R. Roberts, Dr. D. D. Thompson, Catesby Jones, Kenneth Morrissey, T. L. W. Bailey, Jr., and R. B. Sanford. The untiring help of the personnel of the Institute's textile-testing laboratory and of the Research Secretarial Staff is also gratefully acknowledged.

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A Progress Report on Cyanoethylated Cotton[1]

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Abstract

The mechanism of cyanoethylation of cotton is discussed, and it is shown that for best efficiency the pick-up of sodium hydroxide must not exceed 15% of the weight of the cotton.

Measurements of physical properties show that any increases in the breaking strength or elongation of yarns are results of changes in frictional forces. The physical properties of cyanoethylated fabrics reflect the properties of the yarn and are also dependent on fabric construction. Extremely high resistance to flat abrasion is obtained with high cyanoethyl substitution.

The density of cyanoethylated cotton is shown to be linearly related to the nitrogen content, and the spread of values obtained has been found to give an estimate of the uniformity of treatment.

Cyanoethylated cotton can be dyed by methods developed for polyacrylonitrile fibers such as those employing acid dyes in the presence of cuprous ion, and the dyed samples so produced are suitable for cross sectioning for microscopic examination. The intensity of dye color can be used as a measure of the amount of cyanoethylation.

Introduction

The Southern Regional Research Laboratory has for one of its prime objectives the chemical modification of cotton cellulose for the purpose of producing new and better cotton products. Several of the research units of this Laboratory have conducted experiments concerned with the cyanoethylation of cotton cellulose, and the data used in this paper are taken from the reports of these experiments.

In 1953, Dr. Jack Compton, Technical Director of the Institute of Textile Technology, addressed the Chemical Finishing Conference on cyanoethylated cotton [7]. This paper and others [2, 3, 6, 8] have aroused much interest in this method for chemically modifying cotton cellulose. This interest is manifested by large-scale investigations conducted by several of the more prominent chemical manufacturers and mills, and it is, of course, obvious that they have collected and assembled information.

In an attempt to avoid presentation of information already in the literature, data collected at the Southern Regional Laboratory only will be used. In a few cases where repetition of determinations is made for the purposes of drawing conclusions and offering suggestions, the authors believe that they will be found to be confirmatory.

Since the mechanism of the cyanoethylation reaction is of primary importance, one phase will be discussed here.

We shall attempt to throw further light on the physical properties of cyanoethylated cotton by comparing the properties of fibers, yarns, and fabrics.

The dyeing characteristics of cyanoethylated cotton will be shown to be similar in some respects to those of polyacrylonitrile fibers, and an adaptation has proved useful for the purpose of microscopic examination of cross sections.

The relationship between fiber density and degree of cyanoethylation will be shown to be linear, and a method will be suggested for the rapid determination of uniformity of treatment.

Materials and Methods

Fibers for single-fiber tests were obtained by defibering treated yarns, and those destined for heat degradation were washed in water before being placed in the oven to remove contaminating materials acquired during the handling necessary for defibering.

The yarns which were subjected to cyanoethylation were a 12/5 sewing thread with 5 ply twists to the inch and a 16/2 yarn with 8 ply twists to the inch. The single twists of these yarns were not known, but the 12/5 was obviously a tightly twisted yarn, while the 16/2 was "mercerization" or loose

[1] A report based on data collected by three operating units of the Southern Regional Research Laboratory: the Chemical Properties and Physical Properties Units of the Cotton Fiber Section, and the Cotton Unit of the Engineering and Development Section.

[2] One of the Laboratories of the Southern Utilization Research Branch, Agricultural Research Service, U. S. Department of Agriculture.

twist. Both yarns were used in the received state, but a sample of the 12/5 was purified by extraction with ethanolamine according to the method of Kettering and Conrad [14], thus making a total of three types of yarn used. These extracted yarns were employed in the mechanism study reported in Figure 1.

Two types of fabric were employed, an 80 × 80 print cloth and a 48 × 48 sheeting. One sample of print cloth was furnished by the Institute of Textile Technology and two were obtained from commercial sources. All were either scoured or kier boiled, and little if any difference was observed in the physical properties of the cyanoethylated products obtained from the three samples of print cloth. The 48 × 48 sheeting was scoured before use.

The acryonitrile was commercial grade used as received.

Nitrogen analyses were conducted by the Kjeldahl method with the elimination of the sulfuric acid digestion step, which was found to be unnecessary.

Density was determined in a density-gradient column [20] by a revised method developed in this laboratory [17].

Cyanoethylation

Yarns were processed by immersing an alkali-treated skein in acrylonitrile maintained at a prescribed temperature for various lengths of time, followed by washing and souring.

Small samples of fabric were treated in a glass apparatus with a capacity of 2 sq yd of fabric and 1 gal of acrylonitrile. The fabric which had been padded with aqueous sodium hydroxide was laminated with glass cloth and rolled into a cylinder. This cylinder was placed in a glass tube through which the acrylonitrile was circulated. The temperature was maintained at 55–60°C, and the time and alkali content were varied to produce samples having various nitrogen analyses.

Large samples of cloth (25–50 yd) were cyanoethylated in a pilot-plant unit designed and operated by the Engineering and Development Section of this Laboratory [12]. The fabric was soaked in 2% NaOH solution containing a wetting agent, centrifuged to 70% wet pick-up, and laminated with glass cloth. This laminate was wrapped about the perforated core of the apparatus. The ends of the roll were sealed, and acrylonitrile was circulated through the roll in a procedure resembling that used in package dyeing. The temperature was controlled between 55° and 60°C, and the circulation maintained for 1 hr with reversal of flow at 10-min intervals. At the end of the reaction time the acrylonitrile was pumped off and the treated fabric washed, soured with acetic acid, and washed again.

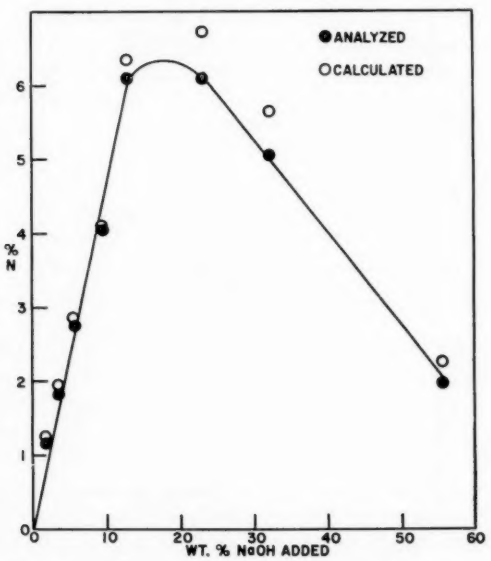

Fig. 1. The effect of sodium hydroxide pick-up on the nitrogen content of cyanoethylated cotton.

The Mechanism of the Reaction

The cyanoethylation reaction is known to be reversible [15, 19, 23], and the reaction is assumed to take place according to the scheme [1] shown in Figure 1*A*.

This mechanism is under investigation at the Southern Regional Research Laboratory, and one phase of the work involves a study of the effect of amount of NaOH catalyst present in the cellulose [10].

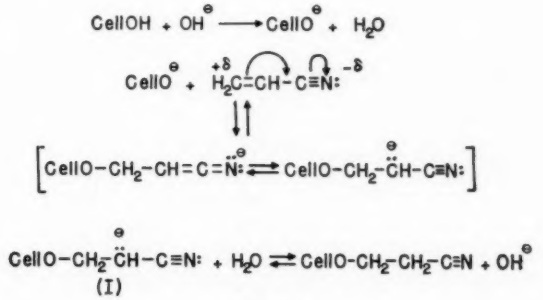

Fig. 1*A*.

Cotton yarns were soaked for short periods in sodium hydroxide solutions of different concentrations and were centrifuged. Pick-ups were determined, and the yarns were allowed to react with acrylonitrile for ½ hr at room temperature. The products were analyzed for nitrogen content; also, the nitrogen content was calculated from the weight gain. Excellent agreement between these two values was obtained (see Figure 1).

It was assumed that the short period used did not allow the cellulose-NaOH system to come to equilibrium, and that the pick-up of NaOH was equal to the total pick-up multiplied by the concentration of the sodium hydroxide in weight per cent.

If per cent nitrogen found in the product is plotted against per cent sodium hydroxide added to the cellulose, a curve is obtained with a maximum nitrogen content at about 15% NaOH take-up (Figure 1).

From the mechanism illustrated it is apparent that the forward reaction is controlled by the concentrations of acrylonitrile and the cellulosate ion, while the reverse rate depends on the concentrations of the hydroxyl ion and cyanoethylcellulose. It is true that the forward rate is also dependent on the concentration of OH^- ions since these are necessary to generate the cellulosate ions. It is probably true that in competition between the cellulose and cyanoethylcellulose for the OH^- ion the preference would be for formation of the cellulosate ion rather than the carbanion (I).

If this is correct, then any NaOH in excess of that which enters into formation of the cellulosate ion would favor production of the carbanion (I) and the reverse reaction, and would result in lower cyanoethyl substitution in the cellulose.

Karrer [13] and others have shown that there is evidence of compound formation between NaOH and cellulose. A ratio of 1 NaOH to 2 anhydroglucose units would require a pick-up of 12.3% NaOH, while a ratio of 1:1 would require 24.7% NaOH. Since the maximum in the curve in Figure 1 is in the neighborhood of 15%, the 1:2 ratio is favored and it is therefore concluded that any NaOH in excess of 15% contributes only to the reverse reaction and a lowering of the efficiency of the cyanoethylation.

Breaking Strength and Elongation at Break

Strength and elongation of fabrics were measured by standard methods, the properties of yarns using an inclined plane tester and those of single fibers by the tester described by Orr and Grant [16].

The breaking strengths of cyanoethylated 12/5 tightly twisted yarn, 16/2 loosely twisted yarn, and

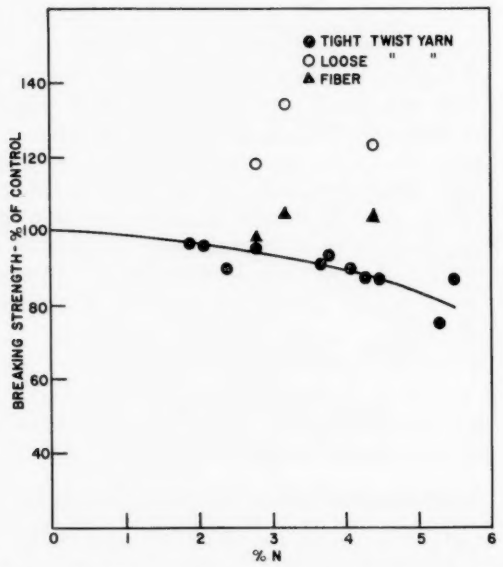

Fig. 2. The relation of breaking strength of cyanoethylated yarns and fibers to nitrogen content.

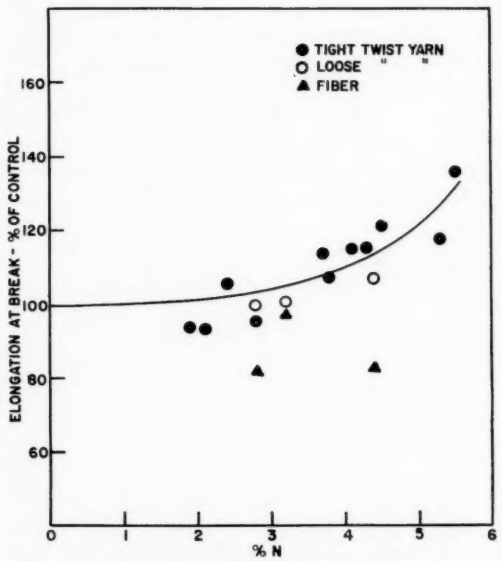

Fig. 3. The relation of elongation at break of cyanoethylated yarns and fibers to nitrogen content.

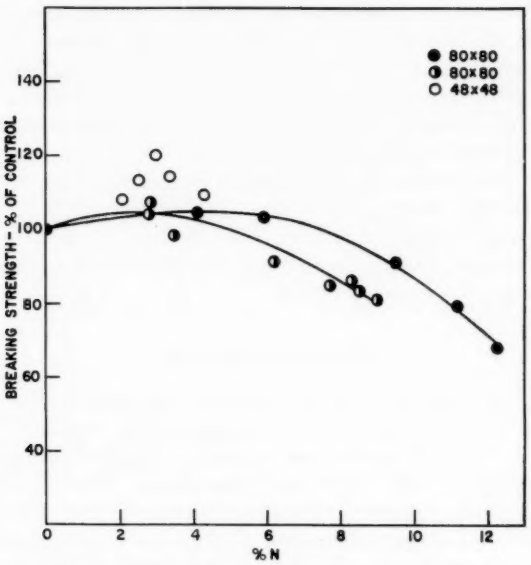

Fig. 4. The relation of breaking strength of cyanoethylated cotton fabrics to nitrogen content.

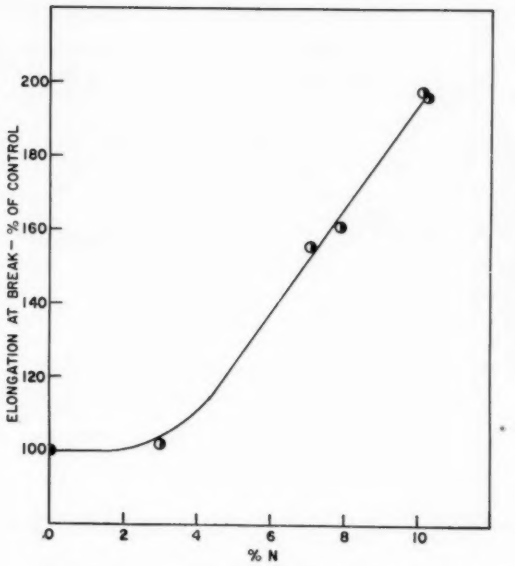

Fig. 5. The relation of elongation at break of an 80 × 80 cyanoethylated fabric to nitrogen content.

single fibers are plotted in Figure 2 against per cent nitrogen found by analysis. From the curve it is apparent that the strength increases in loosely twisted yarns, remains essentially the same in fibers, and decreases in tightly twisted yarns. It is obvious then that the increase in strength of these loosely twisted yarns is due to an increase in frictional forces brought about by changes in yarn construction during the cyanoethylation process. The tightly twisted yarns appear to have little room for improvement in their frictional forces, and the strength gradually decreases with increasing reaction.

The elongations obtained at break for these yarns and fibers are plotted in Figure 3. There appears to be an increase in the elongation of the yarns, while the elongation of the fibers, though variable, shows a small decrease. Here again the increase appears to be due to changes in yarn construction, probably because of the shrinkage acquired when the yarns were treated in the slack condition. This is confirmed by the essentially unchanged length of fibers.

The breaking strengths of three cyanoethylated fabrics are shown in Figure 4. One of these fabrics is the 48 × 48 sheeting, which had a much looser weave than the two samples of 80 × 80 print cloth also plotted in the same figure. Here it is apparent that the loosely woven cloth improved in breaking strength, undoubtedly because its inter- and intra-yarn friction were improved; on the other hand, the tightly woven fabric had no room for improvement, and suffered a gradual decrease in strength with increasing substitution.

It will be noted that the two types of 80 × 80 print cloth showed little difference in breaking strength, and this could probably be explained by differences in fabric construction.

Elongation at break was measured for only one of these fabrics, an 80 × 80 print cloth. Results are shown in Figure 5. The elongation characteristics of the yarns shown in Figure 3 are reflected in this curve. There is little or no change in elongation until about 3% nitrogen content is reached; then the elongation increases rapidly with increasing nitrogen content.

Tear Strength

Tear strengths were determined on two types of treated fabrics by two methods, the trapezoid [22] and the pendulum [21]. The results shown in Figure 6 reflect the properties already discussed. At low nitrogen contents the tear strengths determined by both methods decrease with increasing substitution. This is characteristic of the breaking strength

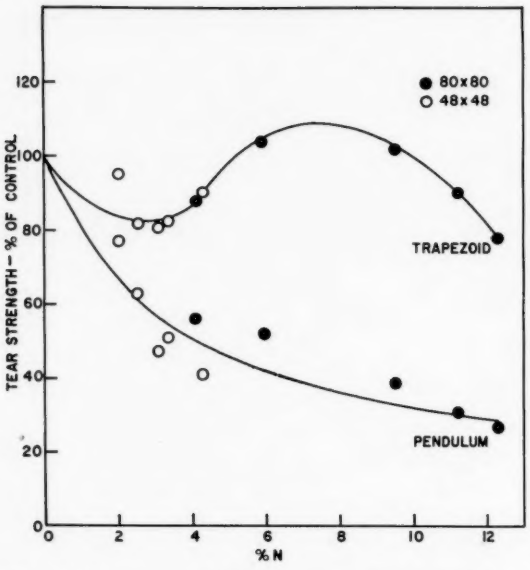

Fig. 6. The relation of tear strength of two cyanoethylated fabrics to nitrogen content.

of the tightly woven fabrics (see Figure 4). However, at about 3% nitrogen content, where the elongation of the yarns and fabric begin to increase (see Figures 3 and 5) the trapezoid tear test begins to show a gain in tear strength. This is probably due to a better distribution of the load over the yarns in the tear area. At about 8% nitrogen content, it appears that the elongation cannot improve the load distribution, and the gradually diminishing breaking strength takes precedence, resulting in another decrease in tear strength.

The pendulum method, employing a high rate of loading, gives a diminishing tear strength with increase in nitrogen content, which differs considerably from the results obtained with the slow loading rate used in the trapezoid test.

Abrasion Resistance

Although the abrasion resistance of cyanoethylated cotton has already been mentioned in the literature [2, 3, 6, 8] the interesting properties of highly cyanoethylated cotton have not been noted. The flex-abrasion properties of cyanoethylated 48 × 48 and 80 × 80 fabrics are shown in Figure 7, while the corresponding results of flat abrasion are given in Figure 8. Both tests were conducted on the Stoll [3] Abrader, using standard procedures, and results are plotted as cycles withstood per hundred cycles of the sodium hydroxide-treated control.

[3] The mention of trade names or manufacturers is not to be construed as a recommendation by the U. S. Department of Agriculture over equivalent products or other companies.

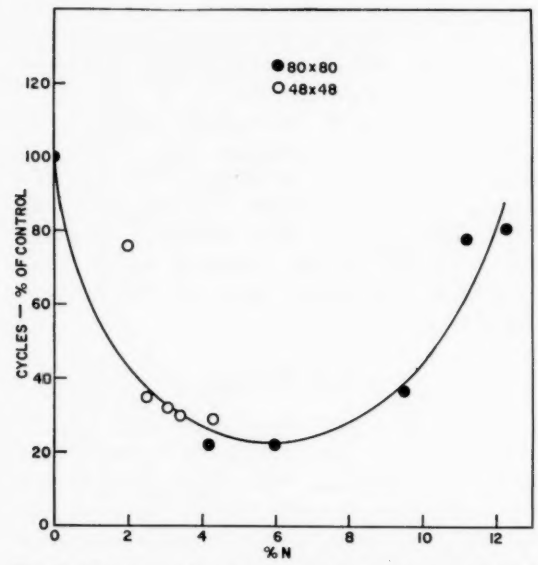

Fig. 7. Relation of flex-abrasion resistance of cyanoethylated fabrics to nitrogen content.

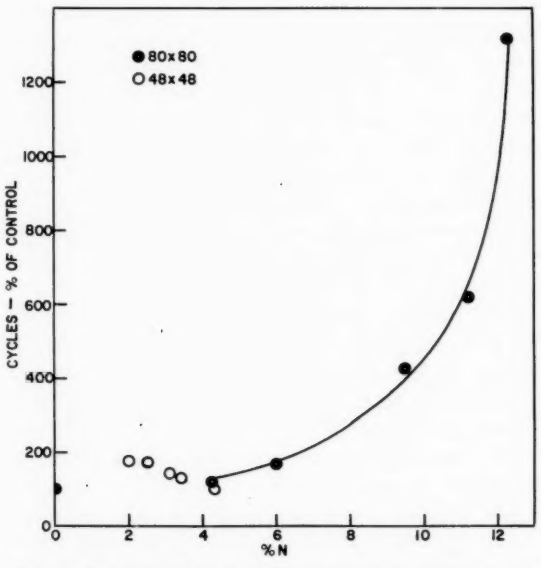

Fig. 8. Relation of flat-abrasion resistance of cyanoethylated fabrics to nitrogen content.

TABLE I. Wet and Dry Heat Resistance of Cyanoethylated Fibers, Yarns, and Fabrics

		% of Original Breaking Strength Retained					
		160°C 1.5% R.H.			160°C 45% R.H.		
Material	% N	1 Day	1 Week	3 Weeks	1 Day	2 Days	1 Week
Fibers	3.2	—	47	—	—	—	37
	4.4	—	56	—	—	—	56
16/2 yarn	0.0	28	14	—	26	19	0
	2.8	55	25	—	56	46	34
	3.2	59	28	—	64	51	30
	4.4	83	50	—	88	84	53
12/5 yarn	0.0	23	11	—	23	18	—
	2.8	47	23	—	50	46	—
	3.8	66	31	—	74	68	—
	4.5	84	40	—	91	83	—
	5.5	70	26	—	85	78	—
48×48 sheeting	0.0	64	18	0	—	—	—
	2.5	89	34	11	—	—	—
	3.4	90	49	15	—	—	—
	4.3	91	45	14	—	—	—

Under flex abrasion, treated fabrics show a sharp decrease in resistance until about 4% nitrogen content is reached, after which there is a correspondingly sharp rise in resistance. It appears, however, that the original resistance of the control fabric is not regained.

When the fabrics are abraded in the flat condition, nitrogen contents up to 4% give variable results, indicating some increase in resistance; but when a content of about 4% nitrogen is reached there is an extremely rapid increase in resistance of the cyanoethylated fabric with further substitution, reaching over 1200% that of the control fabric with a fabric containing about 2.7 cyanoethyl groups per glucose unit (12.3% nitrogen).

Wet and Dry Heat Resistance

The heat resistance of cyanoethylated fabrics and yarns has been noted by Compton [2, 3, 6, 8]. Similar data, shown in Table I, are included only for the purpose of rounding out the discussion of physical properties. From this table it will be noted that in the strength columns in which comparisons may be made the results obtained appear to depend only on the amount of substitution which has occurred. For example, at 4.5% nitrogen, fibers, yarns, and fabrics exposed for 1 week to 160°C dry heat retain about 50% of their strength. There appears to be little difference in the strength retained during wet and dry heating of yarns or fibers.

Resistance to Loss of Strength during Soil Burial

Resistance of cyanoethylated cotton to soil burial was noted by Compton [2, 3, 6, 8], and some of the authors' data are included here for comparative purposes.

Samples of cyanoethylated 12/5 yarns were buried in a bed composed of ⅓ topsoil, ⅓ sand, and ⅓ well-rotted horse manure, maintained at a temperature of 90°F, and well watered. The activity of the bed remained constant throughout the trial period, i.e., it would reduce a control sample to zero strength in 5–6 days. The *p*H remained at about 6.5 throughout the period. The breaking strengths retained for various samples of the treated yarn are shown in Table II. The yarns containing 3.8% or more nitrogen were stable to 22 weeks of burial; and considerable resistance to rotting was shown even at 2.1% nitrogen.

TABLE II. Resistance of Cyanoethylated 12/5 Yarns to Soil Burial

	% of Original Breaking Strength Retained			
% N	3 Weeks	6 Weeks	12 Weeks	22 Weeks
2.1	94	83	48	18
2.8	103	100	72	68
3.8	108	99	103	97
4.5	108	104	101	101
5.5	99	97	101	101

Density Variation

If the density of small samples of cyanoethylated cottons is determined with a gradient column, and plotted against nitrogen content, a linear relationship is immediately evident (Figure 9). The scatter of observations about this line indicates that the accuracy of estimation is about 0.2% nitrogen. In the determination of average density of a sample, about 20 individual specimens, weighing from 2 to 4 mg, were selected at random from treated yarns or fabrics and the density value for each specimen was recorded. The spread from the mean of values for these specimens has been found to give an estimate of the uniformity of treatment. In comparison with untreated cotton, in which the standard deviation of density values is usually less than ±0.0006 gm/cc, the standard deviations for cyanoethylated cotton usually range between ±0.0025 and ±0.0400 gm/cc. These limits of standard deviation are equivalent to ±0.1 and ±1.7% nitrogen contents. Since the test specimens are very small, nonuniformities in chemical treatments which might not be detected by ordinary chemical analysis can be detected by this method. The nitrogen content, N, in per cent, can be estimated from the density by means of the equation

$$N = 66.6 - (42.9 \times \text{Density})$$

Dyeing Properties

It has been found [18] that, in general, methods employed in the dyeing of polyacrylonitrile fibers, such as Dynel and Orlon [3] (Du Pont's acrylic fiber) can be applied to cyanoethylated cotton of low substitution, particularly Blaker's modification [4, 5] of the cuprous-ion method developed by Feild and Fremon [11].

Acid dyes which are not also substantive dyes for cotton and which contain preferably only one sulfonic acid group, such as Fast Red S Conc. (C.I. 176, National Aniline), and Orange II (C.I. 151, Eastman Kodak Co. # 196)[3] give impressive results when applied from an acid bath containing cuprous ion and a reducing agent.

These dyes cause only slight discoloration of untreated cotton, which is increased to an extremely light shade by the presence of cyanoethyl groups. Perceptible dyeing in the presence of cuprous ion is obtained with cyanoethylated cotton containing as little as 0.5% nitrogen or 1 cyanoethyl group for every 17 anhydroglucose units of the cellulose. Extremely dark shades result when the nitrogen content exceeds 2.0%.

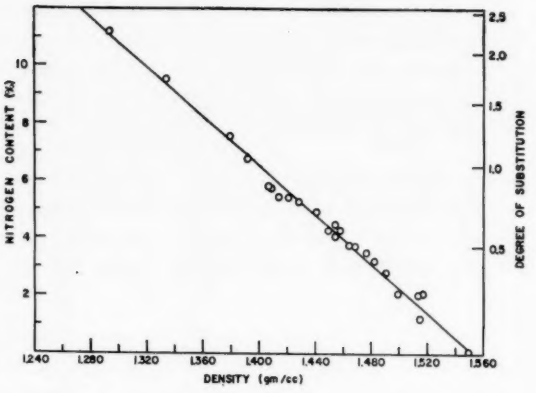

Fig. 9. The relation of density of cyanoethylated cotton to nitrogen content.

Basic dyes such as Du Pont's Basic Blue OB, Basic Red 4G and Basic Yellow OL,[3] which do not dye cotton, will dye cyanoethylated cotton from a bath containing sodium acetate and acetic acid, as recommended by Crawford [9]. Although only a slight amount of color is obtained with cotton containing 2.0% nitrogen, extremely bright shades result when the nitrogen content exceeds 4%.

Microscopic Examination

The dyeing of cyanoethylated cotton with the cuprous-ion technique has been found to be particularly applicable to microscopic examination for the purpose of determining uniformity of treatment. Yarns dyed by the method mentioned display in their cross sections areas of color the intensity of which is apparently directly proportional to the amount of cyanoethylation which has occurred in that area. This is illustrated in Figure 10, which shows a cross section of a cyanoethylated cotton yarn dyed by the cuprous-ion technique using Fast Red S Conc. (C.I. 176, National Aniline [3]). The nonuniformity of the dyeing is obvious, indicating nonuniformity of cyanoethylation.

This yarn had a nitrogen content of 3.71% (3.65, 3.77).

Measurements with the gradient column gave an average density of 1.466, corresponding to a nitrogen content of 3.71%. The extremes in density noted were 1.410 and 1.493 gm/cc, corresponding to ni-

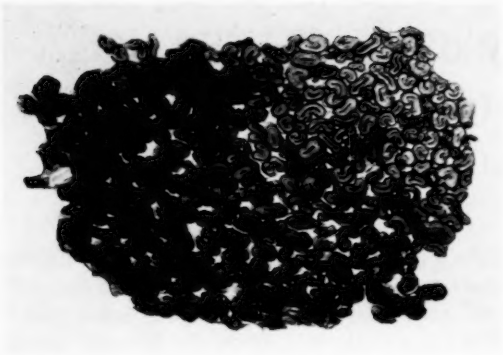

Fig. 10. Cross section of cyanoethylated cotton yarn dyed by the cuprous-ion technique (×250).

trogen contents of 6.11 and 2.55%. The reliability, i.e., the mean ± 1 standard deviation gave a density of 1.444–1.488 gm/cc, or 4.65–2.76% nitrogen. This yarn retained 92% of its original strength after 22 weeks of soil burial and 20% of its original strength when heated at 160°C for 1 week.

Yarns cyanoethylated in a package dyer by the Institute of Textile Technology showed an even distribution of cyanoethyl groups, as did the low- and high-substituted yarns treated in the slack condition in flasks or in tubes with constant flow. Intermediate substitutions, i.e., containing 4 to 8% nitrogen, were sometimes poorly distributed when treated in flasks. It is probable that rapid flow of the acrylonitrile, preferably under pressure, prevents local overheating and is essential for good distribution of the cyanoethyl groups.

Acknowledgment

The authors are indebted to Dr. Jack Compton, Technical Director of the Institute of Textile Technology, for furnishing fabrics, dyes, and much information and advice throughout the course of the investigations reported here.

Cross sections and photomicrographs were made through the courtesy of Miss Mary L. Rollins and members of her Microscopical Properties Unit. Dr. Ruby K. Worner and members of her Unit conducted the physical testing of fabrics and yarns, and Mr. Julian F. Jurgens carried out the Kjeldahl analyses reported here. To all of these the authors owe a debt of gratitude.

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A Preliminary Study of the Dyeing of Cyanoethylated Cotton

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Introduction

Cotton as a textile fiber possesses an array of highly desirable qualities. Many of these are dependent upon the structure of the cotton fibers themselves. There are, however, certain fiber qualities which are highly desirable and which are not possessed by cotton. The possibility of obtaining these added desirable qualities and at the same time retaining the inherent advantages of the natural cotton fiber has been quite an attractive challenge. As a result, different modifying processes for cotton fibers and fabrics have been developed. Two of the most promising of these are acetylation and cyanoethylation. As a result of work done at the Institute of Textile Technology (ITT) in particular, the cyanoethylation process has received a considerable amount of publicity in the past 2 years.

The essential chemistry of the cyanoethylation reaction is relatively simple and has been the subject of many different studies [1, 2, 5, 7]. It involves simply the introduction of cyanoethyl groups onto some of the glucose units of the cellulose by an ether linkage. This occurs by reaction with hydroxyl groups in the cellulose:

$$\text{Cell—OH} + \text{CH}_2{=}\text{CH—CN} \longrightarrow \text{Cell—O—CH}_2\text{—CH}_2\text{—CN}$$

Such a modification has the advantage of preserving the basic architectural structure of cotton cellulose in the new fiber. The extent to which the properties of the cellulose are modified depends upon the number of cyanoethyl groups introduced, or, as more commonly expressed, upon the degree of cyanoethylation. The studies of Compton and coworkers [4] have shown that a cyanoethylation treatment which provides 3.5% of nitrogen in the fiber, an average of approximately 0.46 cyanoethyl groups per glucose unit, results in enough improvement in some of the properties of the cellulose to have considerable commercial promise. Two of the outstanding advantages of such material are resistance to heat and resistance to rotting.

As a part of the studies carried out at ITT, some attention was given to the dyeing of the cyanoethylated material. In general, it was found that the fiber had considerable affinity for different classes of dyes. Compton [3] expressed the dyeability in terms of the amount of dye required to produce a given depth of shade, and using these terms he found the dye requirements were appreciably less for cyanoethylated cotton than for the untreated material. For 7 dyes reported, the amount of dye required to produce a given shade on cyanoethylated material was about 40% less than on untreated material. This excellent study was rather exploratory, however, and did not provide any detailed information on the dyeability of the treated product.

A series of studies has been under way at the American Cyanamid Company laboratory to obtain a more complete story on the dyeing of cyanoethylated cotton. A preliminary observation of the dyeability with the different classes of dyes disclosed that the cyanoethylated material has at least some affinity for each of the different classes studied. Its dyeing properties, however, were found to be different from those of untreated cotton and unlike those of any other natural or synthetic fiber. In other words, from the dyeing standpoint, cyanoethylated cotton must be considered as a different material. In considering the dyeability it is preferable to regard each class of dyes separately. In addition, within a class each dye is best considered individually.

Studies reported by Compton [4] have shown that to obtain the desired improvement in properties the cyanoethylation should be sufficient to introduce approximately 3.5% nitrogen. The major part of our work, therefore, has been carried out with yarn which has been treated to an initial nitrogen content in this range even though better color value might be obtained in some cases on cyanoethylated cotton containing a different amount of nitrogen.

In several cases the dyeing methods were different from those normally employed for the particular type

dyes being used. These deviations from fairly standardized practices were made where it was thought a more valid comparison of the two types of fibers would be obtained by such changes.

Throughout this discussion the percentages given in connection with dyeing processes are based on the weight of material being dyed rather than on the volume of dye bath. For example, 10% sulfuric acid in a 40:1 dye bath corresponds to an acid concentration of 0.25%.

Differential Dyeing Tests

The dyeing properties varied considerably, depending upon the degree of cyanoethylation. This variation was the basis of dyeing tests which were set up to differentiate between samples. In their study of cyanoethylation, the Southern Regional Laboratory found that Calco Stain No. 2 gave a good indication of the degree of modification. This stain was developed to differentiate among the members of a more complex group of fibers than is encountered in cyanoethylated cotton. The simple combination of Calcomine Blue DR and Calcomine Scarlet 3B, which has been established and used by ITT, serves quite well to differentiate between different degrees of treatment and has been adopted in the American Cyanamid laboratory along with a second test using a mixture of Calcomine Blue DR and Calcosyn Brilliant Scarlet BN. Both of these combinations dye untreated cotton blue and cyanoethylated cotton, having 5% or more nitrogen, red. Intermediate stages of treatment become colored to shades ranging between blue and red depending upon the degree of conversion. The first combination, Blue DR and Scarlet 3B, is preferred for differentiating between treatments amounting to less than 2% nitrogen, while the second, Blue DR and Brilliant Scarlet BN, shows better differentiation at nitrogen contents from 2% to 5%.

Vat Dyes

Exhaustion and color value. The cyanoethylation of cotton should upgrade the quality, particularly the durability. As a result it will be desirable to obtain dyeings of the highest quality. Because of their superior fastness properties the vat dyes were selected as the first class of dyes for a careful study. In addition there were some preliminary indications that, because of the strongly alkaline dye baths, the vats might present more dyeing problems. The initial studies of the application of vat dyes to cyanoethylated cotton were carried out in the Dyeometer [6] with samples of cotton cyanoethylated at ITT to an extent of 3.5% added nitrogen. The curves of Figures 1 to 6, inclusive, show the exhaustion characteristics of the cyanoethylated yarn compared in each case with an untreated sample from the same lot. Some of the samples had been given a softening treatment after being cyanoethlated. In all cases the exhaustion characteristics of treated and softened yarn and of yarn treated but not softened were the same. It can be seen that with each of these dyes the cyanoethylated fibers absorbed the dye more rapidly and exhausted the bath more completely than the untreated material.

The color value obtained in beaker dyeings of the treated cotton was also greater than was obtained on the untreated yarn or fabric. The relative color values of some fabric dyeings are given in Table I. All were 10% dyeings made with 1 oz/gal caustic and hydro, run at 140°F for 45 min. In these cases the fabric penetration was quite poor. The concentration of dye in the surface fibers helped to give these dyeings their added strength.

In order to examine more thoroughly the dyeing properties of the vat colors, representative dyes were applied to skeins of untreated cotton and to cyanoethylated cotton (3.5% nitrogen). The results of the tests are summarized in Table II. This table shows the color values of the dyeings, the washfastness to AATCC Cotton Wash Test No. 3, and the lightfastness, on both treated and untreated cotton.

It can be seen from the values in Table II that the cyanoethylated yarn generally dyed heavier than

TABLE I. Color Values of 10% Beaker Dyeings on Cyanoethylated Cotton (3.5% Nitrogen) *

Dye	Color Value of Dyeings	
	Untreated Cotton	Cyanoethylated Cotton
Vat Pink FF Double Powder Pr 109	100	190†
Vat Blue BLD Double Powder CI 1113	100	150
Vat Yellow GCD Double Powder Pr 9	100	125
Calcosol Gray 2G Double Paste	100	130
Vat Navy Blue Paste CI 1100	100	145

* Dyed for 45 min at 140°F in a vat dye bath containing 1 oz/gal caustic and hydro.
† Pronounced difference in shade.

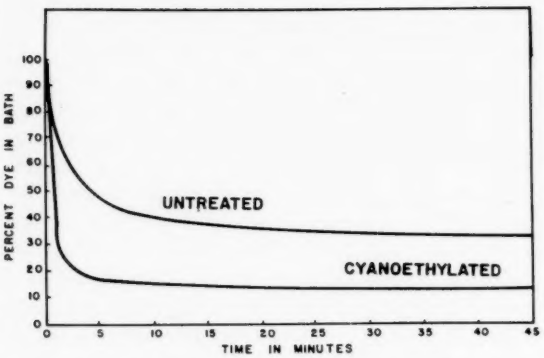

Fig. 1. 4.0% Vat Pink FF Double Powder Pr. 109.

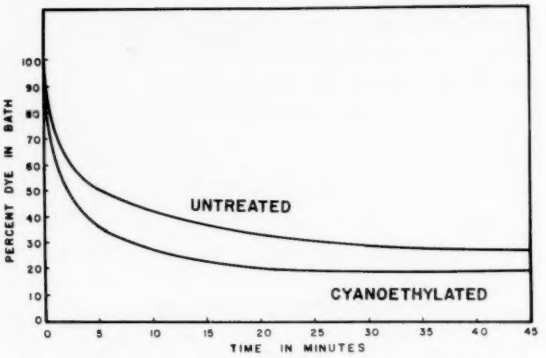

Fig. 2. 6.0% Vat Blue BLD Double Powder CI 1113.

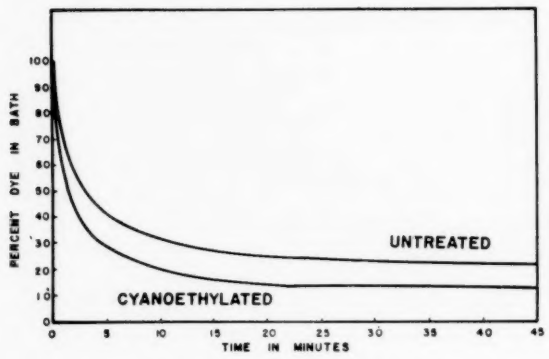

Fig. 3. 4.0% Vat Yellow GCD Double Powder Pr 9.

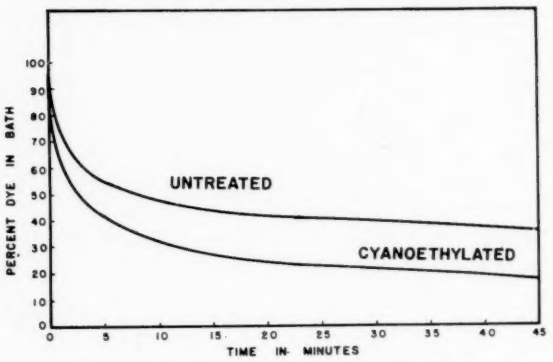

Fig. 4. 4.0% Calcosol Gray 2G Double Paste.

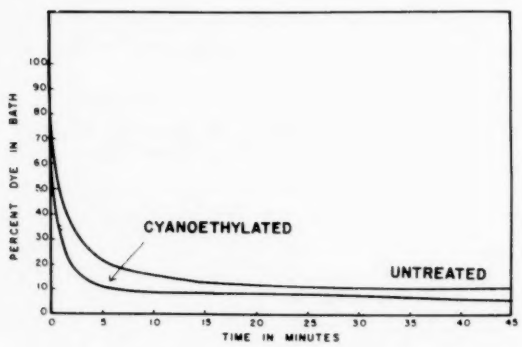

Fig. 5. 4.0% Vat Navy Blue Paste CI 1100.

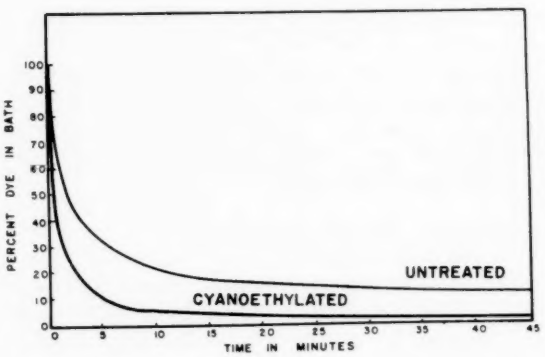

Fig. 6. 4.0% Calcosol Jade Green N Supra Double Paste CI 1101.

Exhaustion rates of vat dyes on untreated and cyanoethylated cotton (3.5% nitrogen) at 140°F. Bath ratio 80:1. Concentration 1 oz/gal caustic and hydro (0.5 oz/gal caustic and hydro used for Jade Green).

TABLE II. 5.0% Beaker Dyeings of Vat Dyes (Double Strength) on Cyanoethylated (3.5% Nitrogen) and Untreated Cotton *

Name of Dye	Color Value† Cyanoethylated (3.5% N)	Cotton Wash No. 3		Lightfastness	
		Untreated	Cyanoethylated (3.5% N)	Untreated	Cyanoethylated (3.5% N)
Vat Blue BLD CI 1113	160	H 5 S 4–5	5 4–5	6+	6+
Calcoloid Copper Brown	230 much yell.	H 5 S 4–5	4 sl. red 5	6+	5
Vat Brown G CI 1152	210	H 5 S 4–5	5 4–5	6	6
Vat Violet 6RD CI 1212	210	H 5 S 4–5	5 4–5	5	6–7
Vat Blue BOD CI 1099	150	H 4 sl. red S 5	4–5 sl. red 5	6–7	6–7
Calcoloid Fast Yellow	130	H 5 S 4–5	5 4–5	6	5 sl. red
Vat Pink FF Pr 109	150 yell.	H 4 sl. yell. S 5	4–5 sl. yell. 5	5	5
Vat Yellow GCD Pr 9	100	H 4–5 sl. red S 5	4–5 sl. red 5	5 sl. red	4–5 sl. red
Vat Golden Orange GD CI 1096	100 sl. bri.	H 3–4 yell. S 5	4 sl. yell. 5	6	6
Vat Orange RD CI 1217	250	H 4 sl. yell. S 5	4 sl. yell. 5	4–5	4
Calcoloid Gray 2G	150	H 5 S 4–5	5 4–5	6+	6+
Vat Brown R CI 1151	170	H 5 S 4	5 4	6	6
Vat Jade Green N CI 1101	125	H 4–5 sl. yell. S 5	4–5 sl. yell. 5	6+	6+
Vat Olive Green BN Pr 293	150	H 3 bri. S 5	4–5 sl. bri. 5	6+	6+
Vat Olive T Pr 547	90 yell.	H 5 S 4	5 4–5	6+	6+

H = Change in shade. S = Change in strength.

* Reduced at 140°F for 10 min with 1 oz/gal caustic and hydro. Dyed at 140°F for 30 min.
† The color value of the cyanoethylated cotton is based on untreated cotton as the standard (100%).

the untreated material and the fastness to both washing and light was unimpaired.

Penetration. The very rapid exhaustion of dye may present a problem in certain cases. As might be expected from such extremely rapid exhaustion, the penetration of the dye into the interior of the threads and of the fabric was sometimes rather poor. Cross sections of yarn and fabric dyed in beakers by regular leuco methods showed the outer fibers were heavily dyed and well penetrated, but many of the fibers in the interior often remained undyed. This lack of complete penetration is not uncommon, particularly with rapid exhausting colors on closely woven fabrics or on yarns having a high twist. Apparently as the dye liquor diffuses into the material being dyed the very fast dyeing rate causes the leuco to exhaust into the fibers in the outer portions of the threads and fabric so that little or no dye reaches the inner portions of the structure. This problem was more pronounced with the cyanoethylated cotton than with the untreated material. The penetration considered here is that into the threads and fabric. The penetration of dye into the individual fibers which were dyed was quite good. Efforts to slow down the dyeing rate by the use of retarding or leveling agents led to some improvement in penetration, but the amounts needed were rather excessive. As would be expected their use decreased the color value of the dyeings.

In order to overcome the problem of penetration, tests were made of pigment pad dyeing methods. In this case the fibers were first impregnated with the unreduced pigment form of the dye by padding the fabric in an aqueous dispersion. Reduction and

fixation were accomplished by placing the padded material in a solution of caustic and hydro. Since the dye was distributed into the interior of the fabric before the leuco was formed, the rapid exhaustion of the reduced dye did not contribute to poor penetration. As a result pigment padding methods produced much better penetration into the cyanoethylated fabric than was obtained by regular leuco vat dyeing methods.

Yarn dyed in the laboratory package dyeing machine also has shown considerable penetration of the threads. The method used involved first pigmenting the package with the unreduced dye and then converting the dye to the leuco form by the addition of hydrosulfite. It seems probable that the initial pigmentation of the package along with the high rate of flow obtained in a 1-lb machine enabled the dye to penetrate the threads before the dyeing took place. The problem of package levelness will have to be considered further when larger amounts of material are available.

Stability of treated fiber. Although the cyanoethyl groups are introduced into cellulose in the presence of dilute caustic as a catalyst, stronger caustic, particularly at higher temperatures, is known to remove the cyanoethyl groups from treated material. For that reason, it was necessary to examine carefully the possible effect of the vat dyeing processes on the cyanoethylated material. It is generally considered probable that there is some cleavage of the cyanoethyl groups although there is considerable hydrolysis of the CN to the COOH group. MacGregor [7] reported that, when tricyanoethyl cellulose was boiled with 5% sodium hydroxide, ammonia was liberated. The carboxy groups present in the hydrolysis products accounted for only ¼ of the nitrogen liberated as ammonia, however. This indicated some cleavage must have occurred. The result in either case is the loss of nitrogen. Therefore, in the present study, the amount of nitrogen present was adopted as a measure of the degree of cyanoethylation. It is recognized that this does not take into account any partial hydrolysis to the amide. In all cases the nitrogen was determined by an adaptation of a modified Kjeldahl method used at the Southern Regional Laboratory.

In the first test, samples of treated cotton were dyed for 1 hr at 140°F in a vat dye bath containing 1 oz/gal of caustic soda and 1 oz/gal of sodium hydrosulfite. The results of the nitrogen analyses are given in Table III. It can be seen from these data that the vat-dyeing process caused a loss of cyanoethylation amounting to approximately 0.5% nitrogen. A similar series of samples was subjected to the same dyeing treatment without any dye in the bath. Following this they were dyed by the differential dye test mixture of Blue DR and Brilliant Scarlet BN. The color of each band in a tubing knitted from fiber representing different degrees of cyanoethylation dyed a distinctly bluer shade than was obtained before the vat dyeing treatment. This again supported the analytical observation that the degree of cyanoethylation was less after the vat dyeing process. Another set of samples was heated at 200°F for 1 hr in a solution containing 2 oz/gal of caustic soda. When these samples were dyed with the differential dye mixture, none of the samples showed any red color. This dye test indicated that the removal of cyanoethyl groups had been essentially complete.

Following this, a more careful investigation was undertaken of the effects of the different vat dye bath variables on the degree of cyanoethylation. In separate experiments samples of cyanoethylated yarn containing initially 2.88% nitrogen were heated at 120°F, 140°F, 160°F, and 200°F in baths containing 0.5 oz/gal, 1.0 oz/gal, and 2.0 oz/gal of sodium hydroxide. In each case a portion of the material was removed and analyzed for nitrogen at 10-min

TABLE III. Nitrogen Analysis (% N) of Vat-Dyed Cyanoethylated Cotton *

Original	After Dyeing	Loss
1.26	0.75	0.51
2.31	1.71	0.60
3.05	2.50	0.55
5.17	4.73	0.44

* Dyed for 1 hr at 140°F in a vat dye bath containing 1 oz/gal caustic and hydro.

TABLE IV. Per Cent Nitrogen Remaining on Cyanoethylated Cotton Treated with 0.5 Oz/Gal Caustic Soda
(Initial Nitrogen Content 2.88%)

Time (min)	Temperature			
	120°F	140°F	160°F	200°F
10	2.66	2.70	2.51	1.85
20	2.61	2.51	2.34	1.32
30	2.56	2.59	2.28	0.80
40	2.60	2.55	2.11	0.23
60	2.58	2.39	2.02	0.41

intervals for 1 hr. The results of these analyses are given in Tables IV, V, and VI. The same values are plotted as graphs of the percent of nitrogen vs. time in Figures 7, 8, and 9. Separate experiments showed that the nitrogen loss, at a given temperature and caustic concentration, was essentially unchanged by the presence of hydrosulfite and dye. The results of these analyses are given in Table VII.

In 1 hr at 120°F, only 10% to 15% of the original nitrogen was lost. At this temperature there was practically no difference between the results obtained with the different caustic concentrations.

At 140°F, the loss of nitrogen was only slightly greater than at 120°F for 0.5 oz/gal and 1.0 oz/gal concentrations of caustic. With 2.0 oz/gal, however, the loss in 1 hr was greater and amounted to about 30%.

Increasing the temperature to 160°F resulted in a more pronounced loss of nitrogen. At this temperature the loss was roughly twice that at 140°F.

At a temperature of 200°, the loss after 1 hr at all three caustic concentrations amounted to more than 95% of the original nitrogen.

The loss of nitrogen became greater as either the caustic concentration or the temperature was increased. The separate effects of these two variables observed at the end of 30 min are shown in Figure 10, in which nitrogen content is plotted vs. temperature, and in Figure 11 in which nitrogen content is plotted vs. caustic concentration. This latter plot indicated that the loss of nitrogen was almost directly proportional to the caustic. These results correspond quite closely with those presented in Table VII, in which is listed the per cent nitrogen remaining on cyanoethylated cotton after 30-min vat dyeings with 4% Vat Pink FF, in which varying amounts of caustic and hydro were employed at different temperatures.

In applying vat dyes to cyanoethylated cotton some loss in nitrogen can be expected. By controlling the caustic and the temperature, however, the dyer should be able to keep the loss within predetermined permissible limits.

TABLE V. Per Cent Nitrogen Remaining on Cyanoethylated Cotton Treated with 1.0 Oz/Gal Caustic Soda

(Initial Nitrogen Content 2.88%)

Time (min)	Temperature 120°F	140°F	160°F	200°F
10	2.64	2.62	2.28	1.31
20	2.65	2.51	2.10	0.51
30	2.59	2.36	1.86	0.22
40	2.56	2.28	1.57	0.18
60	2.58	2.04	1.42	0.14

TABLE VI. Per Cent Nitrogen Remaining on Cyanoethylated Cotton Treated with 2.0 Oz/Gal Caustic Soda

(Initial Nitrogen Content 2.88%)

Time (min)	Temperature 120°F	140°F	160°F	200°F
10	2.64	2.42	1.99	0.50
20	2.55	2.38	1.97	0.15
30	2.58	2.08	1.26	0.17
40	2.35	1.87	0.96	0.14
60	2.36	1.70	0.66	0.06

Laboratory Methods for Applying Vat Dye to Cyanoethylated Cotton

No. 1—Pigment Pad Method

The dry fabric was padded, at 160°F, to a wet pickup of approximately 100% in a bath containing the required amount of dispersed vat dye and 0.25% of Deceresol OT (25%).

Reduction	
Bath ratio	40:1
Temperature	140°F
Time	30 min
Concentration	1 oz/gal caustic and hydro
Oxidation	
Bath ratio	40:1
Temperature	140°F
Time	15 min
Concentration	1.3 oz/gal hydrogen peroxide (100 vol) 1.3 oz/gal acetic acid (56%)
Soaping	
Bath ratio	40:1
Temperature	212°F
Time	15 min
Concentration	0.125 oz/gal neutral soap

TABLE VII. Per Cent Nitrogen Remaining on Cyanoethylated Cotton after a 30-Min Vat Dyeing with 4.0% Vat Pink FF Double Powder, with Varying Amounts of Caustic and Hydro at Different Temperatures

(Initial Nitrogen Content 2.88%)

Caustic and Hydro Conc. (oz/gal ea.)	Temperature 120°F	140°F	160°F	200°F
0.50	2.65	2.63	2.48	1.10
1.0	2.62	2.42	2.13	0.37
2.0	2.53	2.20	1.36	0.13

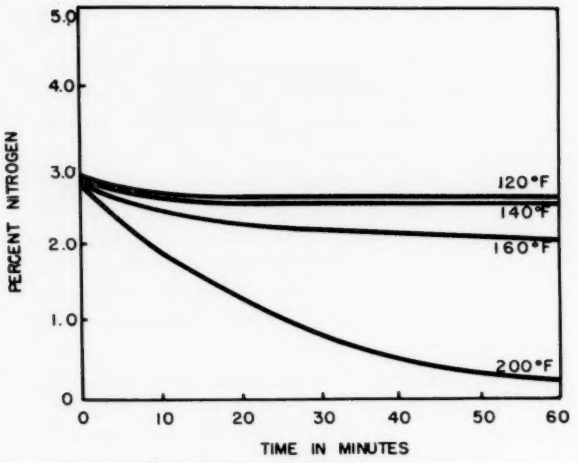

Fig. 7. 0.5 oz/gal caustic soda.

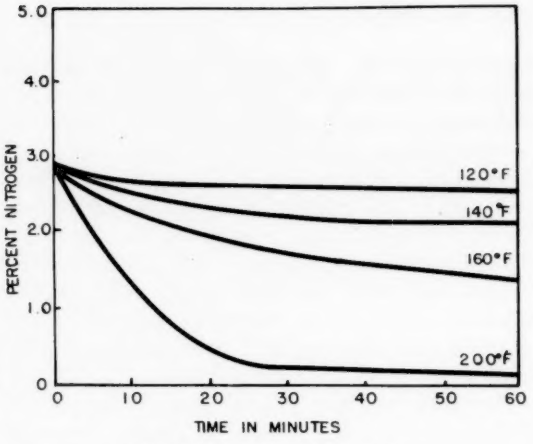

Fig. 8. 1.0 oz/gal caustic soda.

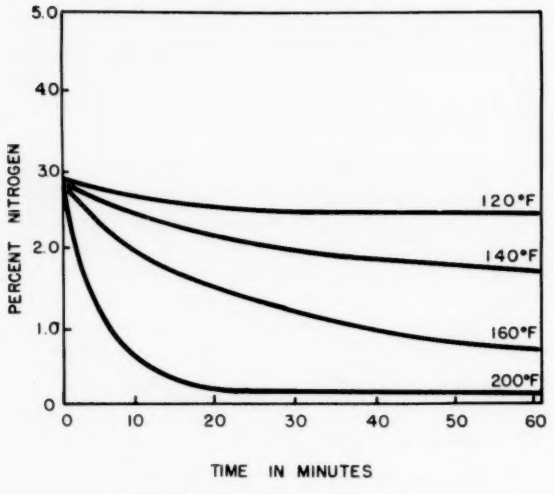

Fig. 9. 2.0 oz/gal caustic soda.

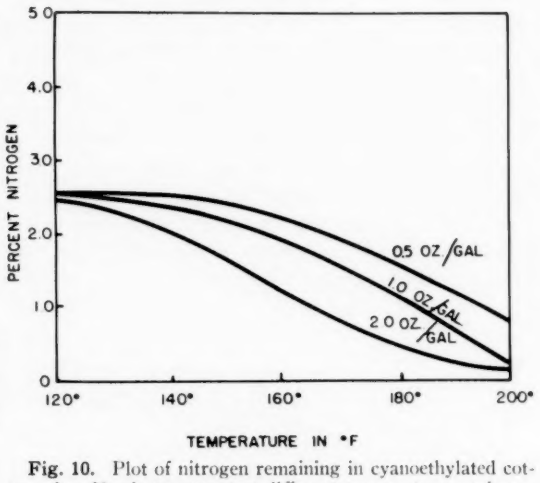

Fig. 10. Plot of nitrogen remaining in cyanoethylated cotton after 30 min treatment at different temperatures and concentrations of caustic soda, nitrogen plotted vs. temperature.

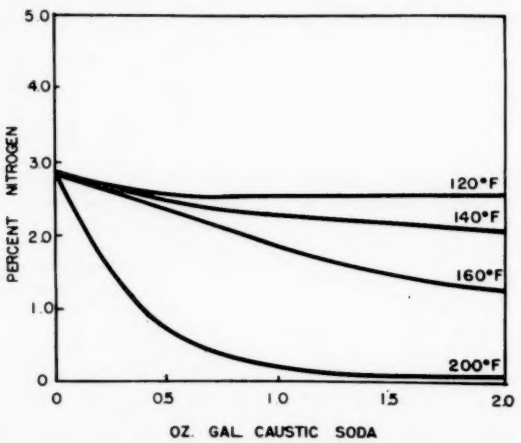

Fig. 11. Plot of nitrogen remaining in cyanoethylated cotton after 30 min treatment at different temperatures and concentrations of caustic soda, nitrogen plotted vs. concentration of caustic.

Graphs showing the rates at which nitrogen is lost from cyanoethylated cotton at different temperatures and caustic concentrations.

Nitrogen analyses on Vat Pink FF dyeings prepared by the pigment pad method above:

Initial Nitrogen (%)	Final Nitrogen (%)	Loss (%)
1.30	1.02	0.28
2.10	1.79	0.31
3.00	2.68	0.32
3.63	3.33	0.30

No. 2—Package Dyeing Method

Weight package	1 lb
Vol. bath	approx. 2 gal

Wet out package for 15 min at 140°F in 1% Deceresol OT (25%).
Required amount of vat dye added, dispersed in a small volume of neutral soap solution.
Pigmented for 20 min at 140°F.
Dye reduced by addition of 1 oz/gal of caustic and 1 oz/gal of hydro. (When dyeing Vat Pink FF the bath was heated to 180°F for 10 min to obtain reduction. It was then cooled to 140°F for the balance of the dyeing.)
Dyed 30 min at 140°F.
Dropped bath, rinsed.
Oxidized with 0.2 oz/gal hydrogen peroxide (100 vol).
When the temperature reached 200°F, added 0.2 oz/gal neutral soap and soaped at 200°F for 20 min.
Flushed, rinsed, dried.
Automatic alternate flow used throughout the dyeing.
All percentages are expressed on the weight of yarn.

Nitrogen Analyses of Package Dyed Yarn

Dye	Initial Nitrogen (%)	Final Nitrogen (%)	Loss
Vat Jade Green	3.55	3.34	0.21
Vat Pink FF	3.55	3.14	0.41

Other Types of Dyes

Although the vat dyes have been considered of greater importance than the other classes of dyes, the study of the dyeability of cyanoethylated cotton has been extended to include a number of representative dyes from other classes. These included the direct dyes, sulfur dyes, naphthol dyes, acid dyes, acetate dyes, basic dyes, soluble vat dyes, and metallized dyes.

In general, cyanoethylated cotton has at least some affinity for each of the different classes of dyes studied. Figures 12 to 17 show Dyeometer exhaustion curves on cyanoethylated and untreated yarn samples for each of six different classes. The rate of exhaustion and also the final exhaust were greater on the treated yarn in most cases.

Microscopic cross sections have been made of the cyanoethylated cotton dyed with each of the above classes of dyes. These cross sections showed complete penetration of the dye into the inner portions of the threads as well as good fiber penetration in all cases.

The Effect of Various Dyeing Processes on Cyanoethylated Cotton

The vat dyeing process involving the use of alkaline baths caused some loss of nitrogen on the cyanoethylated cotton. The other dyeing processes, with the exception of that for the sulfur dyes, did not affect the cyanoethylation treatment to any appreciable extent. The results of the different methods are listed in Table VIII. Immersing the treated yarn in boiling water for 1 hr simulated the dyeing with an acetate or basic dye. Treating the yarn in boiling water containing 20% sodium chloride, or 10% ammonium chloride or sulfuric acid corresponds to dyeing operations for direct or acid dyes, respec-

TABLE VIII. Effects of Various Dyeing Processes on Cyanoethylated Cotton

Treatment	Initial % N	Final % N	Loss
1-hr boil in water	1.04	0.93	0.11
	2.13	2.05	0.08
	2.88	2.75	0.13
	4.90	4.77	0.13
1-hr boil in 20% NaCl	2.13	2.07	0.06
	4.90	4.76	0.14
1-hr boil in 10% NH_4Cl	2.13	2.10	0.03
	4.90	4.90	0.00
1-hr boil in 3% H_2SO_4	1.04	0.92	0.12
	2.13	2.06	0.07
	2.88	2.82	0.06
	4.90	4.74	0.16
1-hr boil in 6% H_2SO_4	1.04	0.97	0.07
	2.13	2.10	0.03
	2.88	2.80	0.08
	4.90	4.77	0.13
1-hr boil in 0.1% soap	2.13	2.09	0.04
	4.90	4.89	0.01
45 min at 200°F in 20% NaCl, 3% Na_2S, 3% Na_2CO_3	1.04	0.34	0.70
	2.13	1.03	1.10
	2.88	1.71	1.17
	4.90	4.01	0.89
1-hr boil in 5% Na_2CO_3	1.04	0.57	0.47
	2.13	1.46	0.67
	2.88	2.03	0.85
	4.90	4.45	0.45

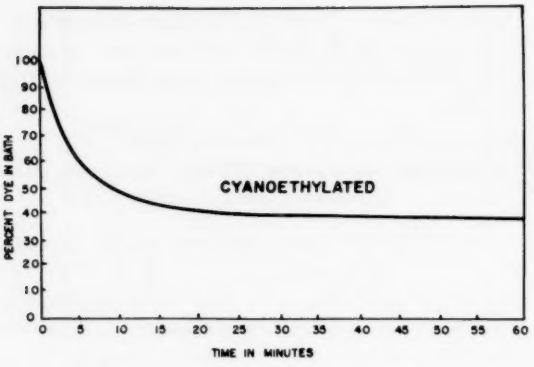

Fig. 12. 5.0% Calcosyn Blue G Pr 62.

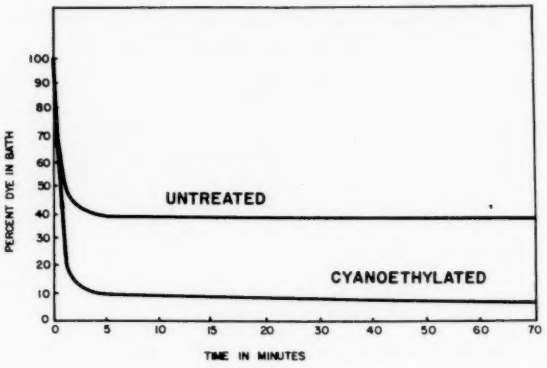

Fig. 13. 0.40% Calcozine Red 6G Extra CI 752.

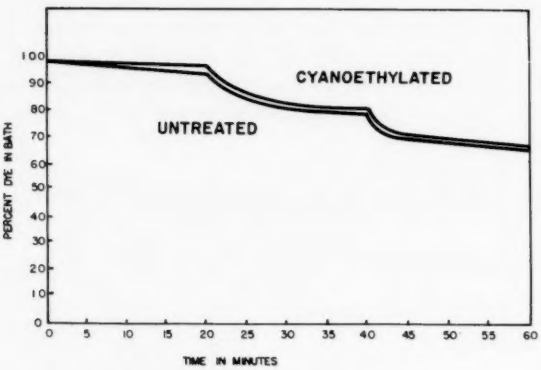

Fig. 14. 2.0% Calcodur Blue SL Pr 71.

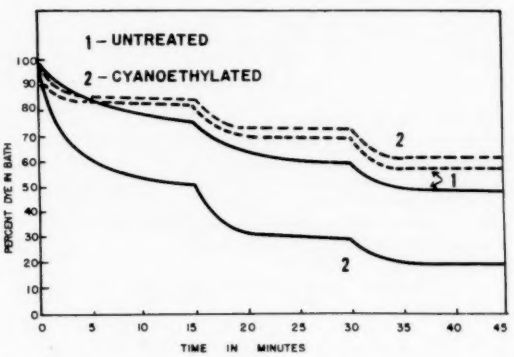

Fig. 15. Dotted lines: 10.0% Calcogene Red Brown EUCF Conc. CI 1012. Solid lines: 10.0% Calcogene Brilliant Green 8G CI 1006.

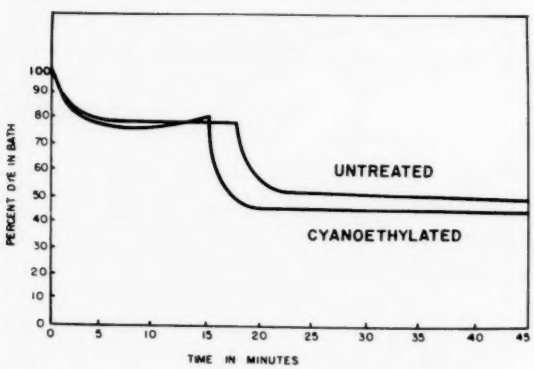

Fig. 16. 2.0% Calcofast Wool Pink N Pr 326.

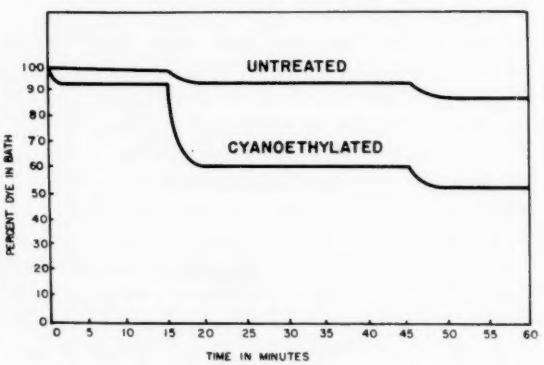

Fig. 17. 2.0% Calcocid Alizarin Blue SBA Pr 12.

Exhaustion rates of various classes of dyes on untreated and cyanoethylated cotton (3.5% nitrogen) at 205–210°F (sulfur dyes applied at 200°F). Bath ratio 80:1. Breaks in curves correspond to additions of common salt.

tively. The differences obtained for the nitrogen content before and after treatment as given in Table VIII are negligible within experimental error and indicate these operations have no effect.

Treating the yarn for 45 min at 200°F in a 20:1 volume ratio dye bath with 20% sodium chloride, 3% sodium sulfide, and 3% sodium carbonate corresponds to an application of sulfur dyes. This caused a loss of approximately 20% of the nitrogen from the fabric that initially contained 4.9% nitrogen.

Direct Dyes

While direct dyes generally do not provide the fastness obtained by the vat dyes, they are widely used because of the ease of application, low cost, and wide selection of available shades.

Twenty-six direct dyes were applied to both untreated and cyanoethylated cotton containing 3.5% nitrogen. The first 13 were random selections without regard to properties. The results of these dyeings and their fastness properties are listed in Table IX. It can be seen that there is considerable variation in the relative color values and fastness properties of these dyes on untreated and cyanoethylated cotton. These preliminary tests indicated that:

1. Out of the first 13 dyes tested, 5 dyed heavier on the untreated yarn, 4 dyed similarly, and 4 dyed heavier on the cyanoethylated cotton.

2. The fastness to AATCC Cotton Wash Test No. 3 was generally similar on the two kinds of material. It was not expected that these dyeings would withstand the No. 3 test. This test was used

TABLE IX. 2.0% Dyeings of Direct Dyes on Cyanoethylated (3.5% Nitrogen) and on Untreated Cotton *

Name of Dye	Color Value† Cyanoethylated (3.5% N)	Cotton Wash Test No. 3‡		Lightfastness		
				Not Aftertreated		Aftertreated§
		Untreated	Cyanoethylated (3.5% N)	Untreated	Cyanoethylated (3.5% N)	Cyanoethylated (3.5% N)
Direct Sky Blue FF CI 518	100 sl. red	H 1	1	3	1	3
		S 1	1			
Direct Orange GL CI 653	100 yell.	H 1	1	5–6	4	5–6
		S 1	1			
Direct Brown M CI 420	115 red	H 5	5	3–4	2–3	3–4
		S 2–3	3			
Calcodur Resin Fast Red 6BL	40	H 2	2	6–7	4–5	6–7
		S 2	2			
Direct Fast Black F CI 539	115	H 1–2	2	3	2	3
		S 1–2	2			
Direct Yellow 2G CI 620	50 greener	H 2	2	1–2 sl. red	1–2 sl. red	—
		S 2	2			
Calcodur Resin Fast Blue 2G	25	H 1	1	5–6	5	—
		S 1	1			
Calcodur Resin Fast Blue 2R	55	H 1	1	6	5	—
		S 1	1			
Calcodur Resin Fast Gray 2G	67	H 2	2	5	4	—
		S 2	2			
Direct Black EB CI 581	125	H 1–2	3	3	2–3	3
		S 1–2	3			
Direct Bordeaux 6BN Pr 67	120 yell.	H 5	3 bluer	3–4	2–3	2–3
		S 3	3			
Direct Fast Violet B CI 387	100 much red	H 1–2	5	5	3–4	5
		S 1–2	2			
Direct Brown BRL Pr 47	100 sl. yell.	H 1–2	1–2	6	4–5	6
		S 1–2	1–2			

H = Change in shade. S = Change in strength.

* Dyed at 200°F for 1 hr in dye bath containing 5% ammonium chloride. 10% common salt added after 10 min at 200°F and an additional 10% common salt after 20 min at 200°F.

† The color value of the cyanoethylated cotton is based on untreated cotton as the standard (100%).

‡ AATCC Cotton Wash Test No. 3 was used to accentuate differences between treated and untreated material.

§ Aftertreated with 1% $CuSO_4$ and 0.5% HAS at 200°F for 30 min.

to bring out any differences between treated and untreated cotton rather than to test the dyes.

3. The lightfastness of this particular list of direct dyes was relatively poor on this cyanoethylated cotton. Nine of the dyeings were given an aftertreatment with copper sulfate and hydroxylammonium sulfate. Aftertreating the dyeings on cyanoethylated cotton in this manner increased the lightfastness in 8 of the 9 cases to equal that on the untreated yarn.

Thirteen additional selected direct dyes were then applied to treated and untreated cotton and tested for lightfastness. As shown in Table X, all of these dyeings without an aftertreatment, possessed lightfastness equal to or better than that on untreated cotton. The results of this test indicate that by a proper selection it should be possible to provide a considerable number of direct dyes that will give good color value, combined with good fastness when dyed on the cyanoethylated cotton.

Three diazotized and developed direct dyes have been applied to untreated and cyanoethylated yarn. Two of the dyes, Direct Diazo Black VJ and Direct Diazo Brown 2RD, gave an increase in color value on the treated yarn, while one, Direct Diazo Green BLD, dyed heavier on the untreated cotton. The fastness of these dyes was similar on the two types of material.

Laboratory dyeing methods for direct dyes. The skeins to be dyed were wet out in water and added to the dye bath made up to a 40:1 volume and contained 5.0% ammonium chloride. The temperature was raised to 200°F, and the skeins were dyed at this temperature for 1 hr. Ten per cent, on weight of fiber, additions of common salt were made at the end of 10 min and 20 min, respectively. The dyed material was given a cold-water rinse and dried.

Aftertreatment. When the dyeings were aftertreated the dyed yarn was treated in a 40:1 bath containing 1.0% copper sulfate and 0.5% hydroxylammonium sulfate at 200°F for 30 min, rinsed, and dried.

TABLE X. Lightfastness of 2.0% Dyeings of Direct Dyes on Cyanoethylated (3.5% Nitrogen) and on Untreated Cotton *

Name of Dye	Lightfastness	
	Untreated	Cyanoethylated (3.5% N)
Direct Green BY CI 593	3	4–5
Direct Blue 4GL CI 533	4–5	4–5
Direct Blue SL Pr 71	5	5
Direct Turquoise GL Pr 278	5	5
Direct Red 8BL CI 278	3–4	3–4
Direct Scarlet B CI 382	2–3	2–3
Direct Orange EGL Pr 72	4	4
Calcodur Orange E3GL	4	4
Direct Resin Fast Orange 5G Pr 578	4–5	5–6
Direct Resin Fast Yellow R Pr 582	5–6	6
Direct Yellow BL CI 814	4–5	5
Direct Yellow 4GL CI 346	4	4–5
Direct Brilliant Yellow CI 365	5	5–6

* Dyed at 200°F for 1 hr in dye bath containing 5% ammonium chloride. 10% common salt added after dyeing 10 min at 200°F and an additional 10% common salt after 20 min at 200°F.

Diazotized and Developed Direct Dyes

The dyeing method for these dyes was exactly the same as the method described above for the direct dyes, except for the diazotization and development treatment. After dyeing, the skeins were rinsed and diazotized in a 40:1 bath with 5.0% sodium nitrite and 2.0% sulfuric acid for 20 min at 70°F, rinsed, then developed with 1.0% Developer Z, 2,4-diaminotoluene or β-naphthol for 20 min at 80° F, rinsed, and dried.

Naphthol Dyes

Different naphthols were applied to cyanoethylated (3.5% nitrogen) and untreated cotton skeins. The naphthols were coupled with a selected list of Fast Color Salts. The color values, washfastness, lightfastness and dry crocking are recorded in Table XI. These results indicate that the naphthol dyes can be applied to cyanoethylated cotton to give increased color value with less dye. This appears to be particularly true for naphthols of low substantivity to cotton. The fastness to Cotton Wash Test No. 3 of the naphthol dyes on the two fibers was similar, while the lightfastness was superior on the cyanoethylated cotton.

It appears that a number of the naphthols of low substantivity, originally used only for padding operations, may be applicable to cyanoethylated cotton by reel or jig dyeing methods. This would increase the variety of shades available and give the dyer a wider selection of dyestuffs.

Laboratory dyeing method for naphthol dyes. The naphthols were dissolved by pasting with Cellosolve and the required amount of caustic soda. Cold water was added to increase the volume to a 20:1 ratio. The well wet-out skeins were added to the

bath and dyed at 85°F for 10 min, after which 20% common salt was added, and dyeing continued at 85°F for an additional 20 min. The skeins were rinsed lightly in salt brine (2 oz/gal common salt), and developed immediately with the Fast Color Salt.

Development. The Fast Color Salts were dissolved in a 40:1 volume bath in cold water containing 2 parts acetic acid (56%) and 0.5 oz/gal sodium acetate. The skeins were developed at 85°F for 30 min, rinsed, and dried.

Sulfur Dyes

As a part of a preliminary study of the dyeing of cyanoethylated cotton, 10 different sulfur dyes were applied to both cyanoethylated (3.5% nitrogen) and untreated cotton skeins. Three dyed weaker on the cyanoethylated yarn, 4 had approximately the same strength, and 3 dyed heavier on the treated yarn. A comparison of the color value, wash- and lightfastness is listed in Table XII. The fastness to Cotton Wash Test No. 3 was quite similar on the two kinds of material. The lightfastness, however, was poorer on the treated cotton.

The poor lightfastness of the sulfur dyes on cyanoethylated cotton was improved by an aftertreatment with copper sulfate, potassium dichromate, and acetic acid, as is also illustrated in Table XII. This portion of the table shows that 3 of the sulfur dyes that originally showed a bad break on the cyanoethylated cotton after 10 hr Fade-O-Meter exposure withstood 20 hr exposure with only a slight break, comparable to the dyeings on untreated cotton.

Dyeing method for sulfur dyes. The sulfur dyes were dissolved with the required amount of sodium sulfide and soda ash. The skeins to be dyed were wet out with water and added to the dye bath made up to a 20:1 volume ratio. The temperature was raised to 200°F, and the skeins were dyed at 200°F for 15 min, after which 20% common salt was added and the skeins were dyed at 200°F for an additional 15 min. The dyed skeins were then given a cold-water rinse and oxidized.

TABLE XI. 4.0% Dyeings of Naphthol Dyes on Cyanoethylated (3.5% Nitrogen) and on Untreated Cotton *

Name of Naphthol	Name of Fast Color Salt	Color Value‡ Cyanoethylated (3.5% N)	Cotton Wash Test No. 3		Lightfastness		Dry Crocking	
			Untreated	Cyanoethylated (3.5% N)	Untreated	Cyanoethylated (3.5% N)	Untreated	Cyanoethylated (3.5% N)
AS Pr 302	†Fast Scarlet R CI 118	180	H 5 S 4	5 4–5	3–4	5	3	3–4
AS-BO Pr 303	†Fast Scarlet R CI 118	200	H 4–5 sl. bl. S 5	5 4–5	4–5	6	3–4	3–4
AS-SW Pr 313	†Fast Scarlet R CI 118	150	H 4–5 sl. yell. S 5	5 5	5	5	4	3
AS-BS Pr 305	Fast Red 3GL Pr 269	300	H 5 S 4	5 4–5	4	6	4	4–5
AS-D Pr 306	Fast Bordeaux GP Pr 260	400	H 5 S 4	5 4	4	6	4–5	4
AS-OL Pr 311	Fast Red B CI 117	250	H 5 S 4	5 4–5	4	6+	4	4
AS-PH Pr 557	Fast Red B CI 117	300	H 5 S 4–5	5 4–5	4	6	4–5	4
AS-BR Pr 304	Fast Garnet GBC CI 17	100 sl. bl.	H 4 sl. bl. S 5	4 sl. bl. 5	6	6	4	3–4
AS-G Pr 309	Fast Red TR Pr 273	110 much red	H 2 yell. S 5	1 yell. 5	3	2–3	4	4–5
AS-RL Pr 312	Fast Red TR Pr 273	135 yell.	H 5 S 4–5	5 4	6	6	4–5	4

H = Change in shade. S = Change in strength.

* Dyed 10 min at 85°F. 20% common salt added and dying continued an additional 20 min at 85°F. Volume 20:1 Developed with 16% Fast Color Salt for 30 min at 85°F.

† 12% Fast Color Salt.

‡ The color value of the cyanoethylated cotton is based on untreated cotton as the standard (100%).

TABLE XII. 4.0% Dyeings of Sulfur Dyes on Cyanoethylated (3.5% Nitrogen) and on Untreated Cotton *

Dye	Color Value† Cyanoethylated (3.5% N)	Cotton Wash Test No. 3		Lightfastness			
				Not Aftertreated		Aftertreated‡	
		Untreated	Cyanoethylated (3.5% N)	Untreated	Cyanoethylated (3.5% N)	Untreated	Cyanoethylated (3.5% N)
Sulfur Yellow SCF CI 951	100	H 5 S 3	5 3	3	1	5	5
Sulfur Yellow RCF Pr 130	100	H 3 red S 5	4 sl. red 5	3	2	5	5
Calcogene Olive Yellow KCF	100	H 2 red S 4–5	3–4 red 4–5	4	2	4–5	5
Sulfur Tan YCF CI 948	80	H 5 S 3–4	5 3–4	2–3	1	5	4
Calcogene Dark Brown NCF	100	H 5 S 2	5 2	3	1	5	4
Sulfur Brilliant Green 8G CI 1006	190	H 5 S 4	5 4	4–5	4	5	5
Calcogene Green YSCF	50	H 5 S 3–4	5 3	6	4	5	5
Sulfur Electric Blue CF Pr 65	45	H 5 S 3	5 2	4	1–2	4	3
Sulfur Blue 5RCF CI 959	120	H 5 S 3–4	5 3	6–7	5	4	5
Sulfur Black GXCF CI 978	45	H 3 red S 4	2 red 3	5–6	4	5	5

H = Change in shade. S = Change in strength.

* Dyed at 200°F for 1 hr with the addition of 20% Glauber's salt after 20 min at 200°F.
† The color value of cyanoethylated cotton is based on untreated cotton as the standard (100%).
‡ Hot aftertreatment with 1.5% copper sulfate, 1.5% potassium dichromate, 3% acetic acid (28%) for 30 min.

Aftertreatment. The aftertreatment was carried out in a 40:1 bath containing 1.5% copper sulfate, 1.5% potassium dichromate, and 3% acetic acid (28%) at a temperature of 200°F for 30 min. The skeins were then rinsed and dried.

Acid Dyes

As a portion of the preliminary study on the dyeability of cyanoethylated cotton with acid dyes 12 different acid dyes were applied to cyanoethylated cotton containing 3.5% nitrogen. Although these colors are not applicable to cotton, each one was also dyed on untreated cotton so that the degree of staining could be determined. This brought out the fact that those colors which stained untreated cotton most dyed heaviest on the cyanoethylated yarn.

A visual approximation was also made of the color values of the acid dyes on cyanoethylated cotton as compared to the same dyes on wool. The results of this comparison are presented in Table XIII. These results show that the neutral dyeing types of acid colors have the greatest substantivity to the cyanoethylated cotton. Compared to wool, however, the color value on the cyanoethylated yarn is generally poor.

Since the neutral dyeing acid colors gave better results on the treated material, a group of dyes selected from the neutral dyeing types was applied to the cyanoethylated yarn by both a regular neutral dyeing method and by the cuprous-ion method employing 1.0% copper sulfate and 0.5% hydroxylammonium sulfate. These tests showed that the use of the cuprous-ion method improved the color value with every dye tested, and the lightfastness was improved in several cases. These results are listed in Table XIV.

Laboratory method for applying acid dyes. Method A. The skeins to be dyed were wet out in water and added to the dye bath made up to a 40:1 volume and containing 10% Glauber's salt and 10% ammonium chloride. The temperature was raised to 200°F and the skeins were dyed at 200°F for 1 hr, then rinsed and dried.

Method B. The dyeing method was the same as Method *A* except that 1.0% copper sulfate and 0.5% hydroxylammonium sulfate were added after the skeins had dyed at 200°F for 30 min. The skeins were dyed at 200°F for 30 min after the additions had been made, then rinsed and dried.

Basic Dyes

Six basic dyes were applied to cyanoethylated and untreated cotton both with and without the aid of a mordant. Calco Mordant O was used as the mordant. The results indicated that the cyanoethylated cotton was dyed without a mordant. In some cases, however, the color value was increased to an even greater extent when the fiber was mordanted before dyeing.

In Table XV are listed the color values of mordanted cyanoethylated cotton dyed with basic dyes, as compared to those of untreated cotton which had been mordanted and dyed in the same manner.

TABLE XIII. 2.0% Dyeings of Acid Dyes on Cyanoethylated Cotton (3.5% Nitrogen)*

Name of Dye	Color Value†	Cotton Wash Test No. 3	Lightfastness
Acid Fast Black B CI 307	50	H 5 S 2	3
Calcocid Alizarine Blue SBA	30	H 1 S 1	5
Acid Navy Blue 3R CI 289	30	H 2 S 2	3–4
Wool Blue B CI 209	25	H 1 S 1	1
Acid Yellow BN CI 146	30	H 1 S 1	1 darker
Milling Green 6B CI 667	25	H 1 S 1	2
Alizarine Green CGN CI 1078	25	H 1 S 1	5–6
Acid Fast Light Orange 2G CI 27	2	H 1	2
Milling Orange GSC Pr 151	20	H 1 S 1	2–3
Milling Red 3R CI 275	25	H 1–2 S 1–2	3
Milling Red 7B CI 430	40	H 2 S 2	2–3
Acid Fuchsine 6B CI 57	5	H 1 S 1	1

H = Change in shade. S = Change in strength.

* Dyed at 200°F for 60 min with 10% Glauber's salt and 10% ammonium chloride in the dye bath.

† Visual approximation of the color value of the cyanoethylated cotton dyed with acid dyes, as compared to the same dyes on wool as the standard (100%).

This portion of the table shows that the color values of the basic dyes on cyanoethylated cotton are considerably greater than on the untreated cotton. The fastness properties of the dyeings on cyanoethylated and untreated cotton were similar.

Laboratory dyeing method for basic dyes. The skeins to be dyed were wet out in water and added to the dye bath, made up to a 40:1 volume, containing the dye which had previously been pasted with 1% acetic acid (28%) and 1% Deceresol OT (25%). The temperature of the bath was raised to 200°F, and the skeins were dyed at 200°F for 1 hr.

TABLE XIV. 2.0% Dyeings of Acid Dyes on Cyanoethylated Cotton (3.5% Nitrogen)

	Color Value		Lightfastness	
Name of Dye	Dyeing Method *A*†*	Dyeing Method *B**	Dyeing Method *A**	Dyeing Method *B**
Neutral Black 2B CI 304	100	160	2–3	3–4
Alizarine Gray 2BLS Pr 206	100	300	5	5–6
Alizarine Blue SKY CI 1088	100	300	5–6	5–6
Acid Fast Blue BL CI 833	100	200	4	5–6
Acid Orange RR CI 161	100	140	1	2–3
Alizarine Violet NC CI 1080	100	300	5–6	5–6
Acid Fast Red A CI 176	100	150	1	2–3
Milling Red G CI 443	100	110	1	3–4
Milling Red 3R CI 275	100	125	2	4
Acid Yellow CW CI 801	100	600	1	3–4

* For dyeing method details, see text.

† The color value obtained by Method *A* was arbitrarily assigned a value of 100 for comparison with the results obtained by Method *B*. These values were not compared with wool dyeings.

TABLE XV. 0.5% Dyeings of Basic Dyes on Cyanoethylated (3.5% Nitrogen) and on Untreated Cotton*

Name of Dye	Color Value
Basic Blue GXX CI 922	210
Basic Magenta CI 676	180
Basic Yellow OX CI 655	225
Basic Brown RX CI 332	Much yellower
Basic Violet CI 680	150 greener
Basic Green V CI 657	300

* The color values of basic dyes applied to mordanted cyanoethylated cotton compared to the same dyes applied to mordanted untreated cotton as the standard (100%).

The dyed skeins were then given a cold-water rinse and dried.

Application of mordant. The skeins were mordanted with 2.0% Calco Mordant O in a bath made up to a 40:1 volume and containing 25% common salt. The temperature was raised to 160°F, and the yarn was mordanted at this temperature for 30 min, then rinsed and dried.

Disperse Acetate Dyes

Eleven disperse acetate dyes were applied to cyanoethylated cotton containing 3.5% nitrogen. The color values of these dyeings were compared to those of the same dyes on cellulose acetate. The results as listed in Table XVI show that the disperse dyes on cyanoethylated cotton generally dye within 20% of their strength on cellulose acetate. In this case no effort was made to compare the dyed cyanoethylated yarn with untreated cotton.

Disperse acetate dyes when applied to cyanoethylated cotton generally showed a progressive increase in depth of shade as the degree of cyanoethylation on the fiber increased. This is the basis for one of the differential dye tests to determine the amount of nitrogen on the fiber.

TABLE XVI. 1.0% Dyeings of Acetate Dyes on Cyanoethylated and Untreated Cotton (3.5% Nitrogen)*

Name of Dye	Color Value† Cyanoethylated (3.5% N)	Lightfastness Cyanoethylated (3.5% N)
Calcosyn Yellow MG	80	2–3
Calcosyn Yellow 7G	50	2–3
Acetate Violet R Pr 237	80 bluer	4
Acetate Violet B Pr 241	80	2
Acetate Brilliant Scarlet BN Pr 244	90 duller	2
Acetate Sapphire Blue R Pr 228	90	2–3
Acetate Red GG Pr 236	80 duller	3
Calcosyn Brilliant Rubine R	100 bluer	3
Acetate Orange 3RC Pr 174	90 redder and duller	3
Acetate Pink B Pr 234	90 bluer	4
Calcosyn Orange 6R	90 redder and duller	3–4

* Dyed at 200°F for 1 hr in bath containing 10% Glauber's salt.

† Visual approximation of the color value of the cyanoethylated cotton dyed with disperse acetate dyes, as compared to the same dyes on cellulose acetate as the standard (100%).

The lightfastness of the disperse dyes on cyanoethylated cotton is also listed in Table XVI.

Laboratory dyeing method for disperse acetate dyes. The skeins to be dyed were wet out in water and added to the dye bath made up to a 40:1 volume containing 10% Glauber's salt and the dye which, before addition to the bath, had been pasted with 0.5% Deceresol OT (25%). The temperature of the bath was raised to 200°F, and the skeins were dyed at 200°F for 1 hr. The dyed skeins were then given a cold-water rinse and dried.

Soluble Vat Dyes

Four soluble vat dyes were applied to cyanoethylated cotton containing 3.5% nitrogen. This number of dyeings is insufficient to permit any general statements regarding dyeing behavior. These preliminary tests, however, indicate that pastel shades having good wash- and lightfastness can be obtained on the cyanoethylated cotton. In addition, since the soluble vats are dyed in only a slightly alkaline dye bath, the cyanoethylation should not be affected.

Laboratory dyeing method for soluble vat dyes. The skeins to be dyed were wet out in water and added to the dye bath made up to 40:1 volume, containing dye and 20% common salt. The temperature of the bath was raised to the boil, and the skeins were dyed at the boil for 15 min, after which 2% sulfuric acid was added to the dye bath and dyeing continued at the boil for an additional 15 min.

Oxidation. The skeins were oxidized in a 40:1 bath with 2% sodium nitrite and 10% sulfuric acid at the boil for 5 min, rinsed, and soaped.

Premetallized and Chrome Dyes

Four premetallized and 3 chrome dyes were applied to cyanoethylated cotton containing 3.5% nitrogen. Both groups showed some tinctorial value on cyanoethylated yarn. Those colors that tend to tint cotton gave the best results on the cyanoethylated yarn. Compared to wool, however, the color value of the cyanoethylated yarn was generally poor.

Both classes gave the best color value on the cyanoethylated yarn when dyed in a neutral or near neutral dye bath. With the premetallized dyes the color value decreased as the *p*H of the bath was lowered.

The lightfastness of both the chrome and premetallized types tested was generally good, while the washfastness to Cotton Wash Test No. 3 was poor.

Laboratory dyeing method for premetallized dyes. The skeins to be dyed were wet out in water and added to the dye bath made up to 40:1 volume with dye and 10% ammonium chloride. The temperature was raised to 200°F, and the skeins were dyed at 200°F for 1 hr, then rinsed and dried.

Laboratory dyeing method for chrome dyes. The skeins to be dyed were wet out in water and added to the dye bath made up to 40:1 volume with dye, 10% Glauber's salt, and 5% ammonium chloride. The temperature was raised to 200°F, and the skeins were dyed at 200°F for 1 hr, rinsed, and top chromed in a fresh bath made up to 40:1 volume with 1% potassium bichromate and 1% sulfuric acid, top chromed at 200°F for 30 min, then rinsed and dried.

Discussion

Although no large-scale dyeings have been attempted, because of the lack of sufficient cyanoethylated material, it is anticipated that minor modifications of the laboratory methods will produce satisfactory results. It should be emphasized, however, that the dyeing of cyanoethylated cotton is still in an exploratory stage. Only a limited number of dyes and a few methods have been tried. Only actual trials by the mills themselves will establish the detailed dyeing methods for this new fiber. The work at this laboratory is being continued in an effort to develop improved dyeing procedures, to obtain information regarding the theoretical aspects of dyeing cyanoethylated cotton with various types of dyes, and to study further the changes in the treated fiber under certain dyeing conditions.

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Flame-Resistant Cotton Fabrics: An Emulsion Treatment Using an Organic Phosphorus-Bromine Polymer[1]

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Abstract

Flame-resistant cotton fabrics have been prepared by treatment of the fabric with an aqueous emulsion of an organic polymer, prepared from bromoform and triallyl phosphate. The finish is durable to repeated laundering, and when applied with proper plasticization to fabrics of 8–9-oz weight does not materially change other textile properties. The treatment may be applied on conventional textile finishing equipment.

Introduction

Flame-resistant fabrics are defined by Buck [1] as those fabrics which will not support a flame. Considerable interest in such textiles has arisen because the fire hazards involved in modern life could be greatly reduced by suitably resistant fabrics. In military use, in particular, incendiary damage may be minimized by the use of flame-resistant tentage, tarpaulins, and clothing.

A summary of treatments for rendering cotton fabrics flame resistant may be found in a monograph on the subject by Little [3]. Few methods, however, are listed in which the flame resistance is retained when the fabric is subjected to repeated laundering, and those that are listed suffer defects of various sorts. Recently the use of brominated organic phosphate polymers has been patented with the claim that they give permanent flame resistance when applied to cotton fabrics [6]. These products have been found to be effective but for good results must be prepared by a laborious stepwise method and be applied from organic solvent.

In order to avoid these difficulties another type of organic polymer containing phosphorus and bromine has been developed at the Southern Regional Research Laboratory. This can be prepared in a single step in an aqueous emulsion [2]. The polymer may be applied to fabric directly from the emulsion in which it was prepared. A pickup of 18–22% on cotton weighing 8–9 oz/sq yd produces durable flame resistance, and the fabric retains its textile properties largely unchanged.

Preparation of the Emulsion

The reaction involved in the preparation of the emulsion consists of a telomerization of a polybromomethane with an unsaturated organic phosphate. This reaction proceeds in emulsion by a free radical polymerization mechanism producing a stable emulsion of a polymer, or telomer, containing about 8% phosphorus and 40% bromine. The polymer retains some unsaturated groups and can be further polymerized by heat after application to fabric to produce a durable finish.

A detailed description of the chemistry involved in the emulsion preparation will not be presented in this article, but is planned for a separate publication in the near future.

Materials

Bromoform and triallyl phosphate are used as the polybromomethane and unsaturated phosphate, re-

[1] This is a report on one phase of a program of research, on the flame-resistance treatment of cotton textiles, being supported at the Southern Utilization Research Branch by funds supplied by the Office of the Quartermaster General, Department of the Army, and conducted under the general supervision of the Research and Development Laboratories, Philadelphia Quartermaster Depot, Philadelphia, Pennsylvania.

[2] One of the laboratories of the Southern Utilization Research Branch, Agricultural Research Service, U. S. Department of Agriculture.

Effect of Resins on Durability

It has been indicated that the use of thermosetting resins, particularly those of the methylated melamine formaldehyde type, increase the durability of silicone water repellents to washing and dry cleaning. This has been borne out not only in laboratory applications but also in some mill runs. The improved resistance imparted by such resins is evident in slightly higher spray ratings following a washing procedure, but appears to show up more favorably in a series of multiple washing tests.

To illustrate the point mentioned above in regard to improved spray ratings, a series of tests on OG Byrd Cloth was carried out, using Hydro-Pruf with and without a methylated melamine formaldehyde resin. In this series, figures were obtained also of the tensile strength on the samples of fabrics subjected to tests. Table VI gives the results in detail.

It will be noted from Table VI that the slight improvement in washing resistance due to the presence of the resin was compensated by a somewhat greater loss of strength on the samples where the resin was used.

TABLE VII. Data on Physical Tests on Treated and Untreated Cotton Byrd Cloth

Apply Hydro-Pruf and cure according to standard practice. Determine spray rating, tensile strength, tear strength, and abrasion resistance.

	Untreated	Treated
Hydro-Pruf	—	6%
Cobelfix	—	2%
Spray rating		
Original	—	100
Tensile strength		
Warp average (lb)	169	155
Filling average (lb)	77	72
Tear strength		
Warp average (lb)	7.5	8.7
Filling average (lb)	3.9	3.0
Abrasion (in cycles) (Stoll Flex Tester)		
Warp average	292	1788
Filling average	358	1091
Average of warp/filling	325	1440

Evaluation of Physical Properties

One reference (Table VI) has been made on the results of tensile strength on cotton fabrics treated with Hydro-Pruf with and without melamine formaldehyde resins. Generally speaking, cotton fabrics treated with Hydro-Pruf show a somewhat lower tensile strength than that of corresponding untreated fabrics. It has been shown in our laboratory that a part of this loss in many cases may be accounted for by the high temperature of the curing operation. Furthermore, the loss in strength varies considerably depending on the weight and construction of the fabric. However, it is possible to make the statement that in no case where laboratory checks have been carried out, is there an excessive loss of strength due to the presence of the silicone water-repellent composition.

Several series of tests on the abrasion resistance of cotton fabrics treated with Hydro-Pruf with and without thermosetting resins show a marked improvement in abrasion resistance as measured by the Stoll Flex Tester. In cases where Hydro-Pruf alone constitutes the treatment, there is a marked increase in this factor varying from two times to five times the number of cycles. Where thermosetting resins are present, and in this instance reference is made particularly to the urea formaldehyde type, the abrasion

TABLE VIII. Data on Abrasion Resistance on Treated and Untreated Fabrics

Treat cotton Byrd cloth, 50/50 acetate viscose fabric, and 100% viscose fabric with Hydro-Pruf (6%) and Cobelfix (2%) alone, with urea formaldehyde resins alone (20% Rhonite 610 + 3% Resipon C), and also a combination of the Hydro-Pruf and these resins in the same proportions.

Make abrasion tests using the Stoll Flex Tester on all treated and untreated samples. The results in cycles are shown.

	Cotton Byrd Cloth		50/50 Acetate Viscose Fabric		100% Viscose Fabric	
	Warp	Filling	Warp	Filling	Warp	Filling
Untreated	259	257	105	119	392	282
Hydro-Pruf alone	510	416	203	166	359	368
UF resin alone	58	121	33	36	15	18
Hydro-Pruf with UF resins	128	172	41	43	20	30

resistance is increased to some extent over the same fabric treated with the resins alone.

Tables VII and VIII, taken from laboratory reports, give some interesting data on tensile strength and abrasion resistance on cotton Byrd Cloth treated with Hydro-Pruf.

In Table VII, the use of Hydro-Pruf alone indicated a slight loss of tensile strength in the range of from 6% to 8%, which is certainly very nominal. The figures on tear strength are inconclusive since they show a gain in the warp and a loss in the filling in the case of the treated sample. The figures obtained on the Stoll Flex Tester indicate a very high increase in abrasion resistance.

Referring particularly to the figures in Table VIII showing the results on cotton Byrd Cloth, it will be noted that Hydro-Pruf, when used without urea formaldehyde resins, approximately doubles the number of cycles over the figure for the untreated fabric. Where Hydro-Pruf was used with urea formaldehyde resins, the results are better than those with resins alone. From these results it can be stated that silicone water repellents, when used with urea formaldehyde resins, overcome to a partial extent the rather severe loss caused by the resins. In interpreting the results on the several fabrics tested, it should be noted that the amount of urea formaldehyde resin used was unusually high. When the proportion of the resin to silicone is lower, the abrasion resistance is restored to a greater degree.

Hand

One of the important qualities of all textile fabrics is commonly referred to as "hand." This quality, being one of personal likes and dislikes, can only be evaluated by the buyer. Fortunately, the silicones are very versatile materials, and it is possible to produce almost any type of hand along with the added feature of durable water repellency. Therefore, when silicone water repellents are used, it is never necessary to accept an undesirable finish or hand because of the water-repellent feature.

Conclusions

The data presented in this paper indicate that silicone water repellents appear to have a definite place in the finishing of cotton fabrics, as well as cotton blends. There are many outstanding qualities which are desirable for this purpose with very few serious impediments. It is obvious, of course, that products of this type will be more advantageous in some applications than others, but this can only be determined by extended application and careful evaluation. It is hoped that the results demonstrated in this paper, although far from complete in some respects, will stimulate interest in silicone water repellents for use on cotton fabrics, and lead to improvements not only in the silicones themselves and the catalysts for use with them but also in methods of application.

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